

Soil Sample Collection and Analysis Procedures

Guidance Document 4-04

Petroleum Remediation Program

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

The Minnesota Pollution Control Agency (MPCA) Petroleum Remediation Program (PRP) conducts random on-site audits of 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>. The 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>.

I. Field Screening Procedures

A. Headspace Analysis

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

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

B. Petroleum Sheen Test:

The petroleum sheen test is a quick and easy field method that can be used to determine if a soil sample is considered petroleum saturated.

1. Place a small quantity of petroleum contaminated soil in a jar or on a large spoon.
2. Add enough water to break apart and submerge the soil particles.
3. If droplets of product or rainbow sheen are present on the water surface, the soil is considered saturated with petroleum.

II. Soil Sampling Procedures

A. Soil Sampling – Site characterization for investigation purposes

1. Minimize the possibility of cross-contamination by using disposable sampling equipment that is certified as clean for each sample collected. If disposable sampling tools are not available, specify the cleaning procedures used. Wear clean sampling gloves at each sampling point. When using a split-spoon or similar sampler, wash it with a detergent solution (e.g., Liquinox or equivalent), rinse, and dry it before each use.
2. When sampling excavation sidewalls or floors, remove at least one foot of exposed soil prior to collecting the sample to ensure collection of a fresh sample. See Guidance Document 3-01 *Excavation of Petroleum Contaminated Soil and Tank Removal Sampling* for sampling requirements.
3. Collect samples from split-spoon samplers or soil sample liners using a procedure that will minimize losses due to volatilization. Document the procedure in the *Investigation Report Form*. See Guidance Document 4-01 *Soil and Ground Water Investigations Performed during Remedial Investigations* for sampling requirements.
4. Method 5035 is required when sampling soil for volatile contaminants (see MPCA QA Web page, http://www.pca.state.mn.us/programs/qa_p.html). Collect soil samples using coring devices (e.g., cut syringe, EnCore™, or US Analytical's Eazydraw Syringe™ sampler, or other approved coring device) and either put the "cored" soil directly into containers provided by the analytical laboratory (verify that the laboratory has pre-weighed these containers) or place the sealed coring device (for an EnCore™ type sampler) containing the soil in a cooler containing ice/coolants. The correct volume of soil to use in the coring device is established by weighing a similar soil sample before coring the analytical sample. Do not weigh analytical sample into the sample container because doing so can undesirably aerate the soil sample. The holding time is 14 days for soil samples preserved by methanol or frozen in an approved coring device. Samples in a coring device that are not frozen must be extracted within seven days. **Do not retain soil previously used for field screening or soil classification for analytical samples.**
 - a) GRO and VOC samples: Collect total petroleum hydrocarbons Gasoline Range Organic (GRO) and volatile organic compounds (VOCs) according to the Wisconsin Department of Natural Resources Modified GRO method, EPA Method 5035 (per EPA SW-846), and the MPCA Policy on EPA Method 5035. These methods require the use of methanol as a preservative for most sampling. When methanol is used as the preservative, GRO and VOC results can be obtained from the same sample. Approximately 25 grams of soil is commonly preserved with 25 ml of methanol in a tared 60-ml vial. A maximum of 35 grams of soil is allowed to enable a 1:1 ratio of soil to extraction solvent in the sample container. Other sample sizes, such as 5 grams of soil and 5 ml of methanol in a 40-ml VOC vial, can be utilized if the 1: 1 ratio is maintained. An approved sampler (e.g., EnCore™ or similar certified sampler) can also be utilized to hold the samples for 7 days from the date of sampling when held at 4° Celsius, or 14 days from the date of collection when frozen below -12° Celsius before methanol preservation following these protocols. A dry weight vial without methanol preservation is also required for every sample. Clean the vial threads to assure a good seal with the cap provided.

- b) DRO samples: Collect total petroleum hydrocarbons Diesel Range Organic (DRO) samples according to the Wisconsin Department of Natural Resources Modified DRO method. Approximately 25 grams of soil is commonly placed in a tared 60-ml vial without preservative. A maximum of 35 grams of soil is allowed to enable a 1:1 ratio of soil to extraction solvent in the sample container. An approved sampler can also be utilized to hold the sample until it is extracted following the Wisconsin DRO protocols. Collect another vial for dry weight determination on the sample. Clean the vial threads to assure a good seal with the cap provided. DRO samples must be extracted within 10 days and analyzed by the laboratory within 47 days of collection.
5. Label all vials, place in a covered cooler with ice, and transport to the laboratory for analysis. Samples should be kept at a stable temperature near four (4) degrees Celsius. Include a container of water for sample temperature verification (temperature blank). The labels should indicate:
 - a) type of analysis
 - b) name of facility
 - c) monitoring point identification
 - d) name of person collecting sample
 - e) time and date the sample was collected
 - f) name of preservative added, if applicable
6. Samples must be collected, transported, and delivered under chain of custody.
7. Samples not transported or analyzed within the accepted holding time will be considered invalid.

B. Soil Sampling – Characterization for off-site treatment/disposal

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

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

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

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

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

III. Soil Analysis

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. Certification is currently required for fixed based and mobile laboratories analyzing volatile organic compounds (VOCs). Certification for mobile labs must meet the same requirements established by MDH for fixed based laboratories.

If a non-certified mobile laboratory is used for sample screening, ten percent of samples must be split 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. For all sample analyses, unless otherwise noted in this document, use an EPA-approved method or equivalent. Laboratories will submit chromatograms in support of GRO/DRO analyses indicating contamination is present.

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

Table B. Required analyses and laboratory procedures.

Petroleum product	Parameters
Regular Gasoline, Aviation Gasoline	A, B, D
Unleaded Gasoline	A, B
Unused Petroleum Products: Fuel Oil, Motor Oil, Diesel Fuel, Kerosene, Jet Fuels, Mineral Oil/Spirits, Crude Oil, Stoddard Solvents	A, C, G**
Used Oil (e.g., Motor Oil, Other Used Petroleum Products). See Notes 1, 2, and the section on used oil special considerations below.	A, C, E, F, G**
Unknown Petroleum or Hydrocarbons Mixture	A, B, C, E, F, G**
Other Petroleum Products	Site Specific
Hydraulic Fluids	A, C, F*, G**

- A. Volatile Organic Compounds (VOCs) by the most recent MDH-certified version of EPA method 8260 (see Note 5). A target analyte list can be found in Appendix A. If ground water at the site will be analyzed for VOCs, then analyze soil for BTEX/MTBE (only).
- B. Wisconsin Department of Natural Resources Modified Gasoline Range Organics (GRO) Method (see Note 3)
- C. Wisconsin Department of Natural Resources Modified Diesel Range Organics (DRO) Method (see Note 4)
- D. Lead (see Note 6)
- E. Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, and Silver (see Note 2)
- F. Polychlorinated Biphenyls (PCBs) using the most recent MDH-certified version of EPA method 8082 by the Arochlor method (see Note 2). 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.

- G. Polyaromatic Hydrocarbons (PAHs) by the most recent MDH-certified version of EPA method 8270, modified to include the Appendix C list of target analytes.

** Note that the MPCA Project Manager (PM) will determine the need for PAH analysis. Contact the MPCA 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, metal cutting oils, and hydraulic fluids. **Waste oil** means oil that is discarded/spilled before use.
2. During investigation at used oil sites, collect samples for VOCs, DRO, metals, and PCBs, but direct your laboratory to analyze only the VOC and DRO samples initially. If any of these compounds are detected, proceed with analysis of the metals and PCB samples. *Note:* If you are sampling to fulfill soil disposal requirements, analyze samples for all required parameters (VOCs, DRO, metals, and PCBs). See below for special considerations for soil contaminated with used oil.
3. This is a purge-and-trap, gas chromatography (GC) procedure that utilizes a ten component blend of gasoline compounds for the quantification standard. Approximately 25 grams (20-35 gram acceptable range) of soil is collected using a zero headspace method and placed into a tared 60-ml vial containing 25 ml of methanol followed by measuring the total weight in the laboratory. The sample must be cooled to $4 \pm 2^{\circ}\text{C}$ and must be received by the laboratory within four days (EnCoreTM samplers can be held seven days) and analyzed within 21 days of collection. To ensure the extraction of the volatiles, the soil must be sonicated for 20 minutes (ensure the temperature does not exceed room temperature) before samples are analyzed. A methanol trip blank is recommended when using methanol as a preservative as this ensures no contamination is present in the methanol. The method detection limit shall be no more than 10 mg/kg dry weight.
4. This is a solvent extraction, direct injection, GC procedure that includes a ten component blend of typical diesel oil components for a quantification standard. Approximately 25 grams (25-35 gram acceptable range) of soil is collected using a zero headspace method and placed into a tared 60-ml vial followed by measuring the total weight in the laboratory. The samples must be cooled to four degrees Celsius, received by the laboratory and preserved in solvent within ten days, and analyzed within 47 days of collection. The method detection limit shall be no more than 10 mg/kg dry weight. Separate samples are required for GRO and DRO analyses.
5. This is a purge-and-trap, gas chromatography method. Sampling is similar to GRO, see note 3. The reporting limits and quality assurance for all parameters should be based on the most recent MDH-certified version of EPA method 8260. Note that BTEX/MTBE holding time is 14 days and must be sampled using EPA method 5035. If a mobile laboratory is being used for the analysis of soil samples, the mobile laboratory must follow the method specified calibration and quality control procedures required by the referenced method.
6. Sampling for lead is required for fulfilling soil disposal requirements. Specifically, soil that will be treated after its removal that is actually or potentially contaminated with leaded gasoline must be analyzed to determine if it exhibits the toxicity characteristic for lead. If a total lead analysis indicates a level equal to or greater than 100 mg/kg, a Toxicity Characteristic Leaching Procedure (TCLP) must be performed. If the TCLP level exceeds 5 mg/L the soil must be managed as a hazardous waste in accordance with Minn. R. ch. 7045.

Special considerations for soil contaminated with used oil:

This section outlines additional procedures for testing used oil contaminated soil to determine if the soil is considered a hazardous waste. If the soil is considered to be a hazardous waste, the soil must be managed in accordance with Minn. R. ch. 7045.

1. Soil with a PCB concentration above 50 mg/kg is considered to be a hazardous waste.
2. Soil is considered to be a hazardous waste if it is contaminated with any hazardous waste listed in Minn. R. 7045.0135. If the generator of the soil can certify to the satisfaction of the MPCA staff, by previous knowledge or chemical analysis, that the soil is not contaminated with waste listed in Minn. R. 7045.0135 the soil need not be managed as a hazardous waste.
3. If the concentration of total halogenated compounds determined by VOC analysis is greater than 1,000 mg/kg, the soil is presumed to be hazardous waste unless the generator can rebut this presumption to the satisfaction of the MPCA staff, through previous knowledge or chemical analysis.

4. Soil is considered hazardous if it exhibits the toxicity characteristic of any of the following contaminants: *arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, endrin, lindane, methoxychlor, toxaphene, 2,4-dichlorophenoxyacetic acid, and 2,4,5-trichlorophenoxypropionic acid*. Contaminants known not to be present, such as pesticides and herbicides, need not be tested for if the generator certifies to the satisfaction of MPCA staff that the contaminants are not present. Contaminants exceeding levels in Table C are considered to *potentially* exhibit the toxicity characteristic and a complete TCLP must be performed:

Table C. Levels at which TCLP will be required

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

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

Appendix A: Target Analyte List for Volatile Organic Compounds (VOCs)

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

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

Appendix B: Target Analyte List for Polychlorinated Biphenyls (PCBs)

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

Appendix C: Target Analyte List for Polycyclic Aromatic Hydrocarbons (PAHs)

Chemical Name	CAS #	Report Level (mg/kg dry weight)
Acenaphthene	83-32-9	0.001
Acenaphthylene	208-96-8	0.001
Anthracene	120-12-7	0.001
Benzo(a)anthracene	56-55-3	0.001
Benzo(b)fluoranthene	205-99-2	0.001
Benzo(j)fluoranthene	205-82-3	0.001
Benzo(k)fluoranthene	207-08-9	0.001
Benzo(g,h,i)perylene	191-24-2	0.001
Benzo(a)pyrene	50-32-8	0.001
Chrysene	218-01-9	0.001
Dibenz(a,h)acridine	226-36-8	0.001
Dibenz(a,j)acridine	224-42-0	0.001
Dibenz(a,h)anthracene	53-70-3	0.001
7H-Dibenzo(c,g)carbazole	194-59-2	0.001
Dibenzo(a,e)pyrene	192-65-4	0.005
Dibenzo(a,h)pyrene	189-64-0	0.005
Dibenzo(a,i)pyrene	189-55-9	0.005
Dibenzo(a,l)pyrene	191-30-0	0.005
7,12-Dimethylbenz(a)anthracene	57-97-6	0.001
1,6-Dinitropyrene	42397-64-8	0.100
1,8-Dinitropyrene	42397-65-9	0.100
Fluoranthene	206-44-0	0.001
Fluorene	86-73-7	0.001
Indeno(1,2,3-cd)pyrene	193-39-5	0.001

Chemical Name	CAS #	Report Level (mg/kg dry weight)
3-Methylcholanthrene	56-49-5	0.001
5-Methylchrysene	3351-31-3	0.001
2-Methylnaphthalene	91-57-6	0.005
Naphthalene	91-20-3	0.005
5-Nitroacenaphthene	602-87-9	0.010
6-Nitrochrysene	2/8/7496	0.020
2-Nitrofluorene	607-57-8	0.010
1-Nitropyrene	5522-43-0	0.010
4-Nitropyrene	57835-92-4	0.010
Phenanthrene	85-01-8	0.001
Pyrene	129-00-0	0.001
Quinoline	91-22-5	0.001

Web pages and phone numbers:

MPCA staff:	http://www.pca.state.mn.us/pca/staff/index.cfm
MPCA phone:	651-296-6300 or 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
MPCA VIC Program:	http://www.pca.state.mn.us/cleanup/vic.html
MPCA Petroleum Brownfields Program:	http://www.pca.state.mn.us/programs/vpic_p.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 1-800-422-0798