



**COVER SHEET
STANDARD OPERATING PROCEDURE**

Operation Title: Water Sampling at Petroleum Release Sites

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1. APPLICABILITY

This Standard Operating Procedure (SOP) applies to all programs in the Maine Department of Environmental Protection's (MEDEP) Bureau of Remediation and Waste Management (BRWM). It is also applicable to all parties that may submit petroleum data that will be used by the DEP/BRWM.

This SOP is not a rule and is not intended to have the force of law, nor does it create or affect any legal rights of any individual, all of which are determined by applicable statutes and law. This SOP does not supersede statutes or rules.

2. PURPOSE

The purpose of this document is to describe the MEDEP/BRWM procedure for sampling water for the presence of petroleum-related contaminants and other contaminants that may occur at a petroleum release site. These contaminants include Volatile Petroleum Hydrocarbons (VPH), Extractable Petroleum Hydrocarbons (EPH), Total Extractable Petroleum Hydrocarbons (TEPH), Radon, Arsenic, Lead, Lead scavengers, Methyl tert-butyl ether (MTBE), and Per- and polyfluoroalkyl substances (PFAS). Water samples are collected from monitoring wells and water supply wells to determine extent of groundwater contamination and the impact of groundwater contamination on human health at the exposure point. This standard operating procedure (SOP) is designed to be a guideline for collecting water samples from these wells to assure samples are collected in a consistent, appropriate manner that will provide accurate data for making decisions and meeting the data quality objectives of the task.

3. RESPONSIBILITIES

All MEDEP/BRWM Staff must follow this procedure when performing this task. All Managers and Supervisors are responsible for ensuring that their staff are familiar with and adhere to this procedure. MEDEP/BRWM staff reviewing data by outside parties are responsible for assuring that the procedure (or an equivalent) was utilized appropriately.

4. DEFINITIONS

4.1 ARSENIC – A naturally occurring mineral that is used in industrial processes such as pesticide production and can be concentrated as a result of mining and ore smelting. Arsenic occurs naturally in ferric hydroxide minerals present in Maine aquifer materials (soil and bedrock) and can be desorbed from the aquifer and dissolved into groundwater under certain geochemical settings (reduced conditions). Under rare instances the biodegradation of petroleum contaminated groundwater may generate geochemical conditions that results



in reductive dissolution and desorption of ferric hydroxide minerals and liberate arsenic from the aquifer.

4.2 EXTRACTABLE PETROLEUM HYDROCARBONS (EPH) - Massachusetts Department of Environmental Protection's Method for the Determination of Extractable Petroleum Hydrocarbons (EPH). <https://www.mass.gov/guides/compendium-of-analytical-methods-cam#-petroleum-hydrocarbon-methods->

4.3 HYDROCARBON FRACTIONS- EPH/VPH methods report concentrations for specific carbon ranges that represent the remainder of the TPH mixture after the target compound concentrations have been subtracted. The hydrocarbon fractions analyzed by each analysis includes the following:

Hydrocarbon Fraction	Analytical Method
C9-C18 aliphatics	EPH
C19-C36 aliphatics	EPH
C11-C22 aromatics	EPH
C5-C8 aliphatics	VPH
C9-C12 aliphatics	VPH
C9-C10 aromatics	VPH

4.4 HYDROCARBON TARGET COMPOUNDS- EPH/VPH methods report concentrations for specific petroleum target compounds. The specific target compounds include poly aromatic hydrocarbons (PAHs), benzene, toluene, ethyl benzene, xylene, and MTBE. EPH/VPH methods do not analyze for lead or lead scavengers. Lead and lead scavenger compounds must be analyzed using appropriate analyses based on the CSM and Data Quality Objectives.

4.5 LEAD - Lead can be present in groundwater at some petroleum spill sites, high octane racing fuel, aviation gas (AvGas) and at older sites (pre-1986) where leaded motor fuel was stored and spilled.

4.6 LEAD SCAVENGERS - The common Lead Scavenger chemicals are ethylene dibromide (EDB) and 1,2dichloroethane (1,2 DCA).



- 4.7 METHYL TERT-BUTYL ETHER (MTBE) - An alcohol compound added to gasoline (circa 1979-2006) used to boost octane as a replacement for Lead.
- 4.8 PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) - Synthetic (man-made) organofluorine chemical compounds that have multiple fluorine atoms attached to an alkyl chain that includes PFOA, PFOS, GenX, and many other chemicals. PFAS have been manufactured and used in a variety of industries since the 1940s, notably fire-fighting foams. There is evidence that exposure to PFAS can lead to adverse human health effects.
- 4.9 RADON - A colorless and odorless gas present in soils and dissolved in groundwater that is produced from the natural decay of uranium and radium present in Maine bedrock and soils.
- 4.9 SAMPLE LOCATION: The location where the water sample is collected (i.e. kitchen faucet, outside spigot, pressure tank, before filter, after filter, before softener, well head, etc.) at a given sample point.
- 4.10 SAMPLE POINT NAME: The unique name assigned to the sample point that is consistent with the sample point name in EGAD and GIS. The sample point name is used to designate the sample point on the Chain of Custody and associated site maps.
- 4.11 TOTAL EXTRACTABLE PETROLEUM HYDROCARBONS (TEPH) - The fractionation step described in the EPH method can be eliminated to allow for a determination of a Total Petroleum Hydrocarbon (TEPH), and/or to obtain qualitative “fingerprinting” information. While TEPH provides little information on the chemical constituents, toxicity, or environmental fate of petroleum mixtures, it may be a cost-effective screening tool in cases where relatively low concentrations of contamination are suspected.
- 4.12 VOLATILE PETROLEUM HYDROCARBONS (VPH) - Massachusetts Department of Environmental Protection’s Method for the Determination of Volatile Petroleum Hydrocarbons (VPH) <https://www.mass.gov/guides/compendium-of-analytical-methods-cam#-petroleum-hydrocarbon-methods->

5. GUIDELINES AND PROCEDURES

5.1 INTRODUCTION

Correct sampling of groundwater for petroleum and related compounds is essential to the proper investigation of groundwater contamination at petroleum spill sites. Many compounds related to petroleum may be important to add to the Conceptual Site Model (CSM; SOP RWM-PP-006) and Sampling and Analysis Plan (SAP; SOP RWM-PP-007) depending on site-specific criteria. Each well represents a monitoring well for local groundwater and such data must be factored into the groundwater investigation program.



Volatile Petroleum Hydrocarbons (VPH) – Analysis for VPH compounds is important at gasoline and very recent fuel oil, kerosene, or diesel spill sites. VPH analyses should be conducted in accordance with the Massachusetts Department of Environmental Protection’s Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)

https://www.mass.gov/files/documents/2018/02/23/VPH%20GC%20PIDFID_Revision%202_1_February%202018.pdf

Extractable Petroleum Hydrocarbons (EPH) – Analysis for EPH compounds is important at fuel oil, kerosene, and diesel spill sites. All human health related decisions must be made based on EPH analysis because the list of analytes corresponds to the Department’s Petroleum Clean-up Guidelines. EPH analyses should be conducted in accordance with the Massachusetts Department of Environmental Protection’s Method for the Determination of Extractable Petroleum Hydrocarbons (EPH).

<https://www.mass.gov/files/documents/2017/12/21/MassDEP%20EPH%20Method%20-%20May%202004%20v1.1.pdf>

Total Extractable Petroleum Hydrocarbons (TEPH) – Analysis for TEPH compounds can be used as a screening tool at fuel oil, kerosene, and diesel spill sites. Human health related decisions cannot be made based on TEPH analysis. All human health related decisions must be made based on the full EPH analysis because the list of analytes corresponds to the Department’s Petroleum Clean-up Guidelines.

Radon – When a Water Supply Well is found to be contaminated with petroleum compounds above the Remedial Action Guidelines (RAGs), a Granular Activated Charcoal (GAC) filter system is installed in the drinking water system. Radon is a naturally occurring element present in groundwater and at high concentrations can cause the accumulation of radioactive elements in GAC filter systems to a problematic level. Whenever a GAC filter system is installed, a water sample must be tested for Radon to determine if it may cause problematic accumulation of radionuclides in the GAC system.

Arsenic – When a large petroleum spill occurs, biodegradation of petroleum in groundwater may create geochemical conditions leading to reductive dissolution and desorption of ferric hydroxide minerals that may contain arsenic. BRWM staff should analyze for arsenic at sites where there is a large volume of petroleum released, and petroleum has reached, or is likely to reach, the bedrock and/or groundwater.

Lead – Lead can be present in water samples at some petroleum spill sites, older sites where leaded motor fuel was stored and spilled, and past and present high-octane fuel and aviation gas (AvGas) spill sites. Sample for Lead at gasoline motor fuel sites where the spill pre-dates 1986. Sample at sites where the spill happened between 1986 and 1996 depending on whether



the facility stored leaded fuel. Sample sites with discharges after 1996 only if they involve aviation gasoline or high-octane fuel such as racing motor fuel that contain lead or are suspected of containing lead.

Lead Scavengers – Where Lead is likely present as a groundwater contaminant it is important to test for volatile chemicals called Lead Scavengers. These chemicals were added to leaded fuels to prevent lead deposits building up inside internal combustion engines. The common Lead Scavenger chemicals are ethylene dibromide (EDB) and 1,2 dichloroethane (1,2 DCA). Sample for Lead Scavengers at gasoline motor fuel sites where the spill pre-dates 1986. Sample at sites where the spill happened between 1986 and 1996 depending on whether the facility stored leaded fuel. Sample sites with discharges after 1996 only if they involve aviation gasoline or racing motor fuel that contain lead or are suspected of containing lead.

Methyl tert-butyl ether (MTBE) – Beginning in approximately 1979 MTBE was added to gasoline as an octane booster to replace Lead. Its chemical structure causes it to dissolve readily in groundwater after a spill and can travel with groundwater to human health receptors. MTBE is included in a VPH analysis.

Per- and polyfluoroalkyl substances (PFAS) – PFAS compounds are a group of man-made chemicals that includes PFOA, PFOS, GenX, and many other chemicals. They are used in some fire-fighting foams. When a petroleum fire (i.e vehicle fire, structure fire with petroleum) is extinguished with fire-fighting foam some residual foam may enter groundwater along with petroleum spilled from the vehicle.

This procedure includes three attachments, including the following:

- Addendum A- Additional Requirements for the samplings of Per- and Polyfluoroalkyl Substances (PFAS)
- Addendum B - Additional Requirements for the samplings of Radon for the purpose of Managing Groundwater Treatment Systems
- Addendum C - Additional Requirements for Determining the Nature of Arsenic Concentrations in Water Supplies at Petroleum Contamination Sites

5.2 PLANNING

A well-developed CSM (RWM-PP-006) is imperative for effective use of this technique. Prior to conducting any sampling event, a SAP should be developed (SOP RWM-PP-007). During this phase, it is important to identify which petroleum analysis to use and if it is likely that other, non-petroleum, compounds might be present in the groundwater.

5.2.1 EQUIPMENT



A majority of the Petroleum Program monitoring includes private water supply sampling. Below is a list of recommended equipment to have when conducting water supply sampling.

- Bucket (to collect excess water when sampling treatment systems),
- Disposable nitrile gloves (to prevent exposure and/or cross-contamination),
- Flashlight (to enter dark basements/cellars),
- Field Notebook (to record pertinent information),
- Chain of Custody Forms (to document chain-of-custody),
- Label Tags (to label sample points at households with filters),
- Container of clean water (for rinsing),
- Container of Soapy Water (for washing),
- Sample Containers from laboratory
- Fitting and section of hose to attach to spigot

5.2.2 HEALTH AND SAFETY

A site safety plan in accordance with SOP-RWM-PP-071 is required for all site activities, including collecting water samples. Whenever sampling water from any point, at a minimum wear disposable nitrile gloves and safety glasses. Hand and eye protection decrease the chance of dermal exposure and reduces the chance of cross-contamination of samples. Also be aware of physical hazards; treatment systems are usually located in the basement, so make sure to take a flashlight. Watch for overhead hazards such as low ceilings and/or hanging objects. Be especially careful of electrical hazards such as outlets near the sampling area and/or bare wires. Do not purposefully sniff the sample for odors as contaminated water may contain unhealthy levels of volatile compounds. Lastly, try not to splash the water when sampling; splashing contaminated water in the eyes or on exposed skin could be harmful if the water is significantly contaminated. If water supplies are known or suspected to be contaminated, care should be taken to avoid cross-contamination with other water samples being collected as part of the same sampling event.

5.3 PROCEDURE

5.3.1 OVERVIEW

Sampling Water Supplies Without DEP Installed Treatment System

When sampling a water supply well without any treatment system, samples may be obtained from an indoor faucet (kitchen, bathroom, other), or an outside faucet (spigot). If MEDEP has sampled the well previously and conditions have not changed (house renovations, family size, etc.) samples should be obtained from the same location as previously sampled. If MEDEP has not sampled the well before, or if conditions have changed, samplers should inspect the plumbing and select a sample location closest to the pressure tank or pump. Samplers should make sure that the sample point is clean



(i.e., no grease, lead soldering, or other possible contaminants) and that no possible sources of cross-contamination (gas cans, solvents, etc.) are nearby. If a water treatment system (such as radon, sediment filters, or water softeners) is present, the sample should be collected prior to these systems. If sampling from a faucet, remove the aerator; if sampling from an outside spigot, remove existing hoses from the spigot. Run the water on cold at full flow for least ten (10) minutes prior to collecting a sample. Running the water will accomplish two goals. First, it will purge the pipes of any stagnant water; second, it will drain the pressure tank and cause the pump to turn on and start pumping water from the well. This should allow the collection of a representative sample from the well.

Record any observations and/or comments about matters pertinent to the sample location or to the site.

After the water has run for approximately 10 minutes, reduce the flow to facilitate sample collection with minimal aeration and begin filling the laboratory containers. Do not adjust flow rate when collecting an EPH sample to avoid false positive detections related to plumbing grease. See Section 6.4.3 below for special procedures when sampling for EPH or VPH.

Sampling Households With Treatment System(s)

For households with a treatment system installed, samplers should collect samples after the treatment system first (post-treatment), between treatment devices second, and before the treatment system (pre-treatment) last to reduce likelihood of cross-contamination. The pre-treatment samples should be collected before any filter, softener, or other device that the landowner or MEDEP has installed. The plumbing system, including any treatment devices should be purged by turning on a faucet located on the downstream end of the devices. This may be a kitchen faucet, bathroom faucet, or outside spigot. When sampling from a faucet, remove the aerator prior to purging and sampling. Sufficient water should be purged to flush the treatment devices as completely as possible (10-20 minutes depending on the number of devices present). In most situations, purging can continue while samples are being collected at the designated sample points. The sample before the filter system is taken last due to its highest probability of being contaminated. If multiple treatment systems are present, sampling should proceed from point of use to point of entry (clean to dirty), in order to reduce potential for cross-contamination. Care should be taken to accurately label the sample containers with the correct sample location designation (after, before, between filters). Each sample port location should be purged for 10 to twenty seconds to remove stagnant water prior to sample collection. When sampling, it may be appropriate to attach polyethylene tubing to the sampling port and collect purge water in a bucket. Properly preserved laboratory containers should be filled using a flow rate that is appropriate for the type of analysis and container type.



If multiple treatment devices are present, it may be necessary to take more samples. Samplers should take care to accurately identify and label sample locations and associated laboratory containers. Filtration devices can often be bypassed with bypass valves included in the plumbing. When sampling any of these devices, trace the route of the plumbing (pipes) to make sure the sample is being taken from the correct sampling port. Be sure to include contingencies for such devices in the sampling plan.

Once all the samples have been collected at a water supply, remove gloves, and return all plumbing to its original position (aerator back on faucet, all sample ports closed, etc.). Record water meter readings if the residence is equipped with a meter. Be sure to properly record the units of the meter (cubic feet or gallons). The water meter reading will give (in conjunction with the previous reading) the amount of water being used, which is useful in predicting/explaining the breakthrough in GAC filters. Place the samples in a cooler on ice for transport to the laboratory.

Sampling from Monitoring Wells

When sampling from monitoring wells, reference MEDEP SOP# RMW-DR-002, and 003. These SOPs describe the procedures for collecting groundwater samples for investigation and assessment monitoring (MEDEP SOP# RWM-DR-002) and long-term groundwater plume monitoring (MEDEP SOP# RWM-DR-003).

Analysis-Specific Considerations

Volatile Petroleum Hydrocarbons (VPH) – When gasoline is a chemical of concern at the site VPH analysis is used to quantify water contamination from a release. The VPH method produces chemical concentration data to compare to PRGs. The lab method used is Massachusetts DEP VPH. Fill the lab-provided 40 ml glassware with water at a slow enough rate to avoid bubbles and agitation. Glassware comes from the lab preserved with Hydrochloric Acid.

Extractable Petroleum Hydrocarbons (EPH) – When fuel oil/diesel/kerosene are chemicals of concern at the site EPH analysis is used to quantify water contamination from a release. The EPH method produces chemical concentration data to compare to PRGs. The lab method used is Massachusetts DEP EPH. Fill the lab-provided one-liter amber glassware. The glassware comes from the lab preserved with Hydrochloric Acid.

Total Extractable Petroleum Hydrocarbons (TEPH) – When fuel oil/diesel/kerosene are chemicals of concern at the site, TEPH analysis is used as a screening test for petroleum in water from a release. This method does not produce data comparable to Petroleum Clean-up Guidelines. The lab method used is Massachusetts DEP EPH. Fill the lab-provided one-liter amber glassware. The glassware comes from the lab preserved with Hydrochloric Acid.



Radon – Samples should be analyzed using EPA laboratory Methods 913.0 or SM 7500-RN B. Fill the laboratory-provided 40 mL glassware with the sample water in accordance with the procedure outlined in Addendum B of this SOP. Also see Addendum B of this SOP for guidance on interpretation of radon results when managing groundwater water treatment and filtration systems.

Arsenic – Samples should be analyzed using test EPA laboratory Methods 200.7 or 200.8. Fill the laboratory-provided 250-mL plastic bottles with the sample water. Bottles come from the laboratory preserved with Nitric Acid. Arsenic samples should be collected and interpreted in accordance with Addendum C of this SOP.

Lead – Use EPA laboratory Methods 200.7, 200.8 or 200.9. Fill the lab-provided 250 ml plastic bottles with water. Bottles come from the lab preserved with Nitric Acid.

Lead scavengers – Use EPA laboratory Method 8260D for 1,2 DCA and EPA Method 8011 for EDB. Fill the lab-provided 40 ml glassware with water at a slow enough rate to avoid bubbles and agitation. Glassware comes from the lab preserved with Hydrochloric Acid.

Methyl tert-butyl ether (MTBE) – MTBE is included in the analyte list for the VPH testing method. Fill the lab-provided 40 ml glassware with water at a slow enough rate to avoid bubbles and agitation. Glassware comes from the lab preserved with Hydrochloric Acid.

Per- and polyfluoroalkyl substances (PFAS) – The method used is Modified EPA Method 537, with isotope dilution or EPA method 533. Additional analyses for Total Oxidizable Precursors (TOP) using TOP Assay may be necessary, depending on the Data Quality Objectives for the sampling event (see SOP RWM-PP-007). Samplers will also follow Addendum A - Additional Requirements for the Sampling of PFAS, PFOA and PFOS. All water samples will be collected using dedicated PFAS-free sampling equipment. Prior to sampling each location, the sample handler must rinse their hands and don nitrile gloves. PFAS contamination during sample collection can occur from common sources, including food packaging and certain foods and beverages. Proper hand rinsing and wearing nitrile gloves will help to minimize this type of accidental contamination of the samples. Samples collected for PFAS analysis do not have to be headspace free.

5.3.2 PROJECT SPECIFIC CONSIDERATIONS

The introduction and procedures for each contaminant of concern discussed above should be addressed during sampling. Additionally, there are certain situations that require unique sampling methods. For example, when sampling for petroleum hydrocarbons by either the VPH or EPH methods, it may be necessary to collect



samples from spigots at high flow rates to avoid false positive detections related to the plumbing grease present on the threads or in the shut-off valves (faucets). A section of hose fitted with a “Y”-control valve may be required to assure that grease associated with the moving parts of the fixture or spigot is not introduced into the sample by opening or closing the fixture just prior to sampling.

Another example of a unique situation is when tritium is used to investigate the relative age of the groundwater. Samplers need to remove their watches before collecting samples that will be analyzed for tritium (if the watch is a tritium-illuminated type). Special circumstances should be outlined in the sampling plan.

Samples collected for PFAS must follow procedures in Addendum A to this SOP.

Samples collected for Radon must follow procedures in Addendum B to this SOP.

Samples collected for Arsenic must follow procedures in Addendum C to this SOP.

6. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

In order to ensure that the samples are representative of the water at a given sampling point, the sampler must pay close attention to QA/QC procedures. At each household the sampler must be aware of four (4) areas which may be sources of cross-contamination of the samples: 1) samplers hands--wear a new pair of gloves at every residence sampled and at each sample point; 2) sampling order--sample at the least contaminated households first, the most contaminated last; and at the least contaminated point in any filtration system first (post-filter) and the most contaminated point last (pre-filter) 3) self-contamination--make sure the sampling area is free of any possible sources of contamination (grease on the tap, solvent bottles near the sample port, etc.), and; 4) piping--look at the plumbing and pipe materials and note the presence of lead soldering or improper lubrication (i.e. WD-40, oil, etc.) on the pipes. Also, ask the resident if any work had recently been done on the well, plumbing, or any other components of the water system.

For all Petroleum Program sites, duplicate samples should be collected in accordance with the Leaking Underground Storage Tank (LUST) Quality Assurance Project Plan (QAPP). Typically, the LUST QAPP specifies collecting a duplicate sample for petroleum compounds in groundwater for one out of every ten samples analyzed. A duplicate sample should not explicitly be identified on the sample container or chain of custody as a duplicate. Instead a duplicate sample can be identified as a made up surname or address. Identify the duplicate sample and its co-located sample in your SAP and field notes or trip report.

A trip blank (prepared from contaminant free water by the laboratory or by MEDEP staff) should be preserved with the same preservative as the actual samples, stored and transported with the



other samples collected during the sampling event, and then analyzed (along with the other samples) for the appropriate suspected contaminants by the lab. If a sampling event is completed and the trip blank contains contaminants, this indicates that the containers may not have been clean or other QA/QC procedures have failed. In this case, it may be necessary to re-sample.

Samplers should avoid fueling a vehicle until after the samples have been delivered to the laboratory or after securing them in a cooler. Avoid the use of colognes, perfumes and bug sprays on sampling days. In addition, sampling personnel should avoid any contact with inside surfaces of sample containers and covers or caps.

If sample results indicate that contamination is present at unanticipated levels or between filters re-sampling may be warranted. All sample data should be reviewed for possible sources of error before re-sampling the water supply. Re-check all field documentation from the trip to insure the sample identification or sample numbers were recorded correctly in both the field notebook and on the laboratory analysis request sheet and/or chain of custody. If the documentation check fails, go back to the site and re-sample. When re-sampling, be sure to check the plumbing to make sure all valves are properly opened and closed. An open bypass valve would bypass the filters and supply unfiltered raw water to the house.

7. DOCUMENTATION

Sample point naming should remain consistent through out the project, and any necessary changes should be clearly documented in the project file. Monitoring well names are typically assigned at installation. Addresses are best to use when identifying private water supply sample locations.

All sampling activities must be documented and include the following:

- Sample Location Map using the sample point names recorded on the chain of custody
- Site Name, Town, Spill Number
- Names of Samplers
- Date (s) of sample events
- Data Quality Objectives
- Sample Point Name
- Sample Location
- Collection Method
- Laboratory Analyses
- Comments and notes related to the sample locations

Documentation can include Attachment 1 from the SAP (RWM-PP-007), the sample location map from the CSM (RWM-PP-006), and the Chain of Custody for the specific event that provides legible information related to the samplers, sample date(s), and analyses. Alternatively,



a Trip Report following SOP RWM-DR-013 that includes the above listed information can also be used to document a sampling event. Sample custody must be followed as outlined in MEDEP/DR SOP# RWM-DR-012 – Chain of Custody Protocol. Any Petroleum Program-specific chain of custody should include the assigned sample point name, sample location, and sample collection method as stated in the SAP.

8. REFERENCES

RWM-DR-001 Water Sample Collection from Water Supply Wells

RWM-DR-002 Groundwater Sample Collection for Site Investigation and Assessment Monitoring

RWM-DR-003 Groundwater Sampling Using Low Flow Purging and Sampling For Long-Term Monitoring

RWM-PP-007 Sampling and Analysis Plan for Petroleum Sites

RWM-PP-006 Conceptual Site Model for Petroleum Sites

ITRC – 2018, Total Petroleum Hydrocarbons Fundamentals.

<https://tphrisk-1.itrcweb.org/4-tph-fundamentals/>



**COVER SHEET
STANDARD OPERATING PROCEDURE-ADDENDUM**

OPERATION TITLE: DEVELOPMENT OF A SAMPLING AND ANALYSIS PLAN-
ADDENDUM - A – ADDITIONAL REQUIREMENTS FOR THE
SAMPLING OF Per- and POLYFLUORALKYL SUBSTANCES
(PFAS)



1.0 APPLICABILITY

This Standard Operating Procedure (SOP) ADDENDUM applies to all programs in the Maine Department of Environmental Protection's (MEDEP) Division of Remediation (DR). It is also applicable to all parties that may submit data that will be used by the DEP/DR.

This SOP ADDENDUM is not a rule and is not intended to have the force of law, nor does it create or affect any legal rights of any individual, all of which are determined by applicable statutes and law. This SOP does not supersede statutes or rules.

2.0 PURPOSE

The purpose of this document is to describe the MEDEP/DRs requirements for the development of a Sampling and Analysis Plan (SAP) with specific requirements for the sampling of compounds related to Per- and Polyfluoroalkyl Substances (PFASs), including Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS).

Prior to conducting any investigative field work, routine monitoring, post closure sampling or any data gathering/sample collection project, a SAP will be developed that outlines the goals of the activity and methodology to achieve that goal. A well-developed SAP that is reviewed by all field team members will assure that the goals are obtainable, the methodology is consistent, and the data generated will meet the Data Quality Objectives (DQOs) for the project.

Given the ubiquitous nature of PFAS compounds, the low detection levels that are generally requested, and the different methodologies for which these compounds are tested, additional requirements regarding sampling methodology, equipment, and analysis for PFAS compounds should be included as part of the sampling plan and during the sampling event. This document outlines those specific requirements to be included in a PFAS sampling plan and during sampling.

3.0 GUIDELINES AND PROCEDURES

3.1 INTRODUCTION

A sampling and analysis plan, regardless of whether sampling for PFAS compounds or other potential contaminants, should include all the elements in SOP RWM-DR-014 – Development of a Sampling and Analysis Plan. Although not required to be included in the SAP, (as outlined in SOP RWM-DR-014), an assessment of the existing data should be conducted, a site reconnaissance completed, a conceptual site model developed, and data quality objectives determined as part of planning to assure the SAP will meet the goals of the sampling.

The SAP itself should include the goal of the sampling, end use of data, data quality objectives, schedule, sampling methodology, sampling locations, media to be sampled, analytical parameters, and QA/QC samples. Additionally, a site specific health and safety plan may be necessary (see SOP-DR-014) depending on the scope of the sampling event. For example, collection of samples in a large or moving water body, or as part of large sampling effort



involving drilling rigs and/or excavation equipment would require a health and safety plan; residential well sampling would likely not.

3.2 SAMPLING METHODOLOGY/EQUIPMENT

A description of the sampling methodology will be included in the SAP. Generally, reference to an appropriate SOP for the sample methodology will be sufficient. The Division has developed multiple SOPs for sample collection of most media; please refer to the Division of Remediation's Quality Assurance Plan - Attachment B – Data Collection SOPs for a list of all data collection standard operating procedures.

3.2.1 Sampling Methodology

Sampling for PFAS will follow the standard procedures as outlined in the specific sampling method SOPs. In addition, the following task must be included in the SAP and field staff must perform the task as described below to prevent contamination of the sample:

“Prior to sampling each location the sample handler must wash their hands and don nitrile gloves. PFAS contamination during sample collection can occur from several common sources, including food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will help to minimize this type of accidental contamination of the samples.”

It should be noted that samples collected for PFAS analysis do not have to be headspace free.

3.2.2 Sampling Equipment/Supplies/Personal Protective Equipment (PPE)

The low detection limits required for PFAS water analysis and their common occurrence in frequently used items warrant attention to equipment and PPE used for sampling. A sampling equipment list for PFAS projects should follow the material guidelines in Table 1 of Attachment A, avoiding use of LDPE and any Teflon-lined equipment or tubing. If field decontamination of non-disposable equipment is necessary, washing with an approved soap solution, rinsing with DI water and then a rinse with laboratory-supplied PFAS-free water is recommended. New nitrile gloves should be used between locations and activities. Other recommended clothing and PPE requirements are noted in Table 1 of Attachment A.

3.3 Media Sampled/Analytical Parameters

A chart outlining the media collected and sample analysis methodology will be included in the SAP.

PFOA and PFOS are the typical potential contaminants of concern (COCs) at PFAS sites, although laboratory reporting lists may include 12 to 26 PFAS compounds depending upon method and laboratory. An additional analysis that may be warranted is the sum of all PFAS present, either by total extractable fluorinated compounds (TOP analysis) or evaluation of total



fluorine by a method such as proton induced gamma-ray emission (PIGE). Both of these techniques can be followed by analysis of specific compounds, to assess the presence of precursors in environmental media that are not captured by the compound specific methods.

Parameters will be identified by either laboratory analysis methodology number, or generally accepted name of analysis. Given the different methods currently available for sampling PFAS, there must be a clear understanding between the project manager and the laboratory providing the analysis as to what the media sampled, test methodology, and detection levels will be.

Table 1 provides several current methods with their associated media:

TABLE 1
Media/Analytical Methodology

MEDIA	LABORATORY METHOD	HOLD TIME*/ PRESERVATION	ANALYSIS TIME	Reporting List
Drinking Water**	USEPA Method 537	14 days to extraction/Trizma***	28 days after extraction	Method specific
Groundwater	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Surface Water	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Soil/Sediment/sludge	Modified Method 537	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Other (vegetation...)	Modified Method 537	Lab specific	Lab specific	DEP Minibid list ****
Water or Soil	TOP or other total fluorinated analysis	Lab specific/<6°C	Lab specific	Method specific

* Hold times may vary with contracted laboratory

** USEPA 537 is the only certified method for drinking water

*** Trizma needed for samples that may contain residual chlorine from treated water sources

**** Longer reporting lists may vary between laboratories, generally the DEP mini-bid list can be used for comparison to other selected laboratories

Other methods may be appropriate based on the data quality objectives of the sampling project.

The contracted analytical laboratory must be Maine certified to perform any method for which Maine provides certification. The contract lab must be able to accommodate the sample load and perform the analyses within holding times. The contract lab must be able to achieve PQLs, for all analyses, which are below the associated regulatory guideline value.



Deviations can be made from the laboratory method on a site or event specific basis, based on the goals of the sampling, end use of the data, and the data quality objectives. Rationale for deviations from these methods should be described in the SAP and/or the final report.

As with all parameters, containers, preservation, and holding times will be as recommended by the laboratory providing analytical services. Special or out of the ordinary containers or preservation should be noted in the SAP.

3.4 FIELD QC SAMPLES

Sample collection for PFAS analysis does not require specific field QC samples outside the normal requirements.

General recommendations for all sampling include one aqueous field blank, per field event, to be analyzed for PFASs to determine if water samples have been contaminated by sources unrelated to the project area, and to assess the overall field procedures. An equipment blank may be needed if non-dedicated equipment is used. The field blank is typically one bottle of PFAS-free water supplied by the laboratory, which is uncapped and poured to a second bottle. For multi-day events, one blank per day should be considered. If non-disposable equipment is used a PFAS-free water equipment blank is warranted to check field decontamination procedures.

4.0 PFAS SPECIFIC TEMPLATE

In the instances of a PFAS only sampling event, in which samples are being collected from a project which has a history of sampling for other analytes and a well-developed conceptual site model and/or an SAP already exists, a PFAS sampling specific template has been developed which provides the general requirements of a sampling plan. This template can be found in Attachment A of this Addendum.

5.0 REPORT GENERATION

As stated in SOP RWM-DR-014, A Sampling Event Trip Report (SETR) will be developed for every sampling event (see MEDEP/DR SOP# RWM-DR-013). The staff person responsible for developing the SETR will be stated in the SAP. Data obtained as part of the SAP will be assessed in the final report for which the data has been collected.



ATTACHMENT A
PFOA SAMPLING AND ANALYSIS PLAN FORM TEMPLATE

1.1 INTRODUCTION

The introduction will state the objectives of the sampling plan which include:

- Goals of the sampling plan;
- End use of data.

2.0 BACKGROUND INFORMATION

A BRIEF explanation of the background of the Site and/or conceptual site model (CSM) and reason for sampling for PFAS will be presented.

3.0 SITE SPECIFIC HEALTH AND SAFETY PLAN

If determined necessary, a Site-Specific Health and Safety plan (HASP) will be developed and attached.

4.1 SAMPLING METHODOLOGY/ EQUIPMENT

A description of the sampling methodology will be included in the SAP. In instances where a MEDEP/DR SOP is available, reference to SOPs by either name or document number is sufficient.

Prior to sampling each location the sample handler must wash their hands and don nitrile gloves. PFAS contamination during sample collection can occur from a number of common sources, including food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will help to minimize this type of accidental contamination of the samples, particularly when moving pumps, generators or other equipment between sample points.

Some sampling equipment, field supplies, field clothing and personal protective equipment are prohibited when sampling for PFAS. Table 1 outlines the prohibited items. This table must be included in the SOP and field staff informed as to what equipment is allowed.

ATTACHMENT A -
 PFAS SAMPLING AND ANALYSIS PLAN FORM TEMPLATE –
 04/08/2020

Table 1: Summary of Prohibited and Acceptable Items for Use in PFAS Sampling

Prohibited Items	Acceptable Items
Field Equipment	
Teflon® containing materials. Aluminum foil.	High-density polyethylene (HDPE) and stainless steel materials
Storage of samples in containers made of LDPE materials	Acetate direct push liners
Teflon® tubing	Silicon or HDPE tubing
Waterproof field books. Water resistant sample bottle labels.	Loose paper (non-waterproof). Paper sample labels covered with clear packing tape, or lab-applied labels.
Plastic clipboards, binders, or spiral hard cover notebooks	Aluminum or Masonite field clipboards
	Sharpies®, pens
Post-It Notes	
Chemical (blue) ice packs	Regular ice
Excel Purity Paste TFW Multipurpose Thread Sealant Vibra-Tite Thread Sealant	Gascoils NT Non-PTFE Thread Sealant Bentonite
Equipment with Viton Components (need to be evaluated on a case by case basis, Viton contains PTFE, but may be acceptable if used in gaskets or O - rings that are sealed away and will not come into contact with sample or sampling equipment.)	
Field Clothing and PPE	
New clothing or water resistant, waterproof, or stain treated clothing, clothing laundered with fabric softeners, clothing containing Gore-Tex™	Well-laundered clothing, defined as clothing that has been washed 6 or more times after purchase, made of synthetic or natural fibers (preferable cotton). Cotton coveralls are one option that reduces the need for specialized personal clothing.
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex™	Boots made with polyurethane and PVC for wet conditions, or rubber overboots (“chicken boots”)
	Reflective safety vests, Tyvek®, Cotton clothing, synthetic under clothing, medical braces

**ATTACHMENT A -
PFAS SAMPLING AND ANALYSIS PLAN FORM TEMPLATE –
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No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling	Sunscreens - sunscreens that are “free” or “natural”, or UV blocking clothing Insect Repellents - Sawyer permethrin clothing treatment, Deep Woods Off, Insect Shield pre-treated clothing ⁽¹⁾
Sample Containers	
LDPE, glass containers or passive diffusion bags.	HDPE (any media) or polypropylene (only for EPA Method 537.1 samples)
Teflon®-lined caps	Lined or unlined HDPE or polypropylene caps
Rain Events	
Gore-Tex™ or similar breathable coated waterproof or resistant rain gear	Polyurethane, vinyl, wax or rubber-coated rain gear. Gazebo tent that is only touched or moved prior to and following sampling activities
Equipment Decontamination	
Decon 90	Alconox® and/or Liquinox®
Water from an on-site well	Potable water from municipal drinking water supply (if tested as PFAS-free); Lab-supplied PFAS-free water
Food Considerations	
All food and drink, with exceptions noted on the right	Bottled water and hydration drinks (i.e. Gatorade® and Powerade®) to be brought and consumed only in the staging area

(1) Bartlett SA, Davis KL. Evaluating PFAS cross contamination issues. *Remediation*. 2018;28:53–57.

It is recommended that all water samples will be collected using dedicated or disposable sampling equipment where possible. Any re-usable equipment, such as plumbing fittings, that may be needed in certain cases to obtain a sample from the pressure tank tap, should be decontaminated using Alconox/Liquinox soap and rinsed with PFAS-free water prior to use and between locations.

5.0 Sample Locations

A map showing planned sampling locations will be included in the sampling plan. If locations are not pre-determined, the method that samples will be chosen and collected (field observations, random, etc.) will be outlined in the SAP. Field or laboratory compositing procedures will also be described, if applicable.

This section should also indicate sampling collection priority and order, to assure that the most important samples are obtained, and that sampling is generally done from low areas of contamination to higher levels of contamination. It is recommended that critical samples be collected in duplicate.

6.0 Media Sampled

A chart outlining the media collected and sample analysis will be included in the SAP. Table 2 provides several current methods with their associated media:

ATTACHMENT A -
 PFAS SAMPLING AND ANALYSIS PLAN FORM TEMPLATE –
 04/08/2020

TABLE 2
Media/Analytical Methodology

MEDIA	LABORATORY METHOD	HOLD TIME*/ PRESERVATION	ANALYSIS TIME	Reporting List
Public Drinking Water Supply **	USEPA Method 537.1	14 days to extraction/Trizma***	28 days after extraction	Method specific
Groundwater and Private Water Supplies	Modified Method 537 (Isotope Dilution)	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Surface Water	Modified Method 537 (Isotope Dilution)	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Soil/Sediment/sludge	Modified Method 537 (Isotope Dilution)	14 days to extraction/<6°C	28 days after extraction	DEP Minibid list ****
Other (vegetation...)	Modified Method 537 (Isotope Dilution)	Lab specific	Lab specific	DEP Minibid list ****
Water or Soil	TOP or other total fluorinated analysis	Lab specific/<6°C	Lab specific	Method specific

* Hold time of 14 days is specified by DEP

** USEPA 537.1 is currently the only Maine certified method for drinking water, others such as Method 533 will be offered in the future

*** Trizma needed for samples that may contain residual chlorine from treated water sources

**** Longer reporting lists may vary between laboratories, generally the DEP mini-bid list can be used for all projects

Other methods may be appropriate based on the data quality objectives of the sampling project.

The contracted analytical laboratory must be Maine certified to perform any method for which Maine provides certification. The contract lab must be able to accommodate the sample load and perform the analyses within holding times. The contract lab must be able to achieve PQLs, for all analyses, which are below the associated regulatory guideline value.

Containers, preservation, and holding times will be as recommended by the laboratory providing analytical services. Special or out of the ordinary containers or preservation should be noted in the SAP.

7.0 FIELD QC SAMPLES

The specific needs for QC samples for the project will be outlined. General requirements for PFAS sampling events include one aqueous field blank, per field event, to be tested for PFASs to determine if water samples have been contaminated by sources unrelated to the project area, and to assess the overall field procedures. The field blank is typically

**ATTACHMENT A -
PFAS SAMPLING AND ANALYSIS PLAN FORM TEMPLATE –
04/08/2020**

one bottle of PFAS-free water supplied by the laboratory, which is uncapped and poured to a second bottle. An equipment blank should be collected if non-dedicated equipment is used. For multi-day events, one blank per day should be considered, and for large events one blank per 10 or 20 samples is warranted, depending upon the project requirements. All blanks should be collected with laboratory supplied PFAS-free water. A source-water blank is handled like a trip blank, and assesses the laboratory supplied water and sample containers. This blank may be warranted depending on DEP experience with the laboratory or sensitivity of the project.

Additionally, any QC samples that will be collected in the field that are required as part of laboratory QC requirements and to allow data validation will be outlined.

4.9 REPORT GENERATION

A Sampling Event Trip Report (SETR) will be developed for every sampling event (See MEDEP/DR SOP# RWM-DR-013). Staff person responsible for developing the SETR will be stated.



1. APPLICABILITY

This Standard Operating Procedure (SOP) applies to all programs in the Maine Department of Environmental Protection's (MEDEP) BRWM (BRWM). It is also applicable to all parties that provide or oversee the installation or management of granular activated carbon filtration systems at MEDEP remediation sites.

This SOP is not a rule and is not intended to have the force of law, nor does it create or affect any legal rights of any individual, all of which are determined by applicable statutes and law. This SOP does not supersede statutes or rules.

2. PURPOSE

The purpose of this document is to describe the MEDEP/BRWM procedure for sampling water for the presence of radon and interpreting the results for the purposes of managing drinking water treatment systems.

3. RESPONSIBILITIES

All MEDEP/TS Staff must follow this procedure when performing this task. All Managers and Supervisors are responsible for ensuring that their staff are familiar with and adhere to this procedure. MEDEP/TS staff reviewing data by outside parties are responsible for assuring that the procedure (or an equivalent) was utilized appropriately.

4. DEFINITIONS AND ACCRONYMS

4.1 GAC – Granular Activated Carbon A filter media used to remove organic and inorganic contaminants dissolved in water and control odors. GAC is a form of processed carbon designed to have small, micropores to increase surface areas available for adsorption or chemical reactions. GAC is made from raw organic carbonaceous materials such as coconut shells, nut shells, peat, wood, or coal.

4.2 Low-level waste – Nuclear waste that does not fit into the categorical definitions for intermediate-level waste (ILW), high-level waste (HLW), spent nuclear fuel (SNF), transuranic waste (TRU), or certain byproduct materials known as 11e (2) wastes, such as uranium mill tailings. Low-level waste includes items that have become contaminated with radioactive material or have become radioactive through exposure to neutron radiation.

4.3 pCi/L - Picocurie per Liter

4.4 POET – Point of Entry Treatment- A point of entry treatment system is a whole-house (building) water treatment solution at or before the point the water enters the building.



5. GUIDELINES AND PROCEDURES

5.1 INTRODUCTION

When water supplies become impacted with petroleum compounds, a point of entry treatment (POET) system consisting of GAC filters is often installed to remove petroleum contaminants from the water. GAC filters will also remove radon from water. When POET consisting of GAC is to be installed on a water supply, the concentration of radon in the water supply will need to be determined to ensure appropriate filter system location, and to consider the GAC change-out schedule and whether pre-treatment for radon is required. Additionally, when a replacement water supply well is installed at a site, the concentration of radon in that well will need to be determined.

5.2 PLANNING

Prior to conducting any sampling event, a Sampling and Analysis Plan (SAP) should be developed (see MEDEP/TS SOP# RWM-DR-014 - Development of a Sampling and Analysis Plan).

To complete the sampling activities, staff will need appropriate laboratory-provided sample containers, tubing, a hose adaptor, and a bowl or bucket that is large enough to submerge the sample container. When sampling directly from a wellhead it will be important to ensure that the well has been adequately developed, and a water pump, power source, and associated tubing will be required.

5.3 PROCEDURE

5.3.1 OVERVIEW

Those approved to sample water supplies for radon can collect the sample according a method approved by the Maine Department of Health and Human Services (DHHS) Radon Control Program. MEDEP staff will typically collect radon in drinking water samples using the DHHS-approved method outlined in this SOP.

Sample Collection:

When sampling an active water supply for radon, it is best to sample from the pressure tank faucet if accessible. Otherwise collect the sample from a sample port that is unfiltered being sure to remove the aerator and hoses if present. When sampling from a wellhead,



the discharge piping will need to have a valve installed with a barb to attach tubing. The water supply should be purged for 10 minutes prior to collecting the sample.

When it is time to collect the sample, attach the fitting and tubing to the spigot of the pressure tank (or the tubing to the barb on the piping valve) and start to fill the bowl or bucket. As you are filling the bowl or bucket, adjust the flow to eliminate bubbles or agitation. Fill the bucket enough to be able to submerge the sample container in the water. Once the sample container is submerged, insert the tubing into the mouth of the sample container. Flush the sample container twice, then fill the sample container while it is submerged. Cap the sample container while it is still submerged underwater such that the sample does not contain air bubbles. Do not send samples containing an air bubble to the laboratory.

Interpreting Sample Results:

If the radon concentration in the water supply is less than 10,000pCi/L, the carbon filter media in the GAC POET system can be changed out based on breakthrough of petroleum compounds or bacteria buildup in the filters.

If the radon concentration in the water supply is 10,000 pCi/L or greater, radon concentrations should be entered into the Carbdose calculator, or another EPA-approved calculator. Based on the radon concentration and water supply usage, the Carbdose calculator will provide the time that the GAC will become low-level waste (“waste disposal” output) and the minimum distance recommended to limit gamma radiation in living spaces (“safe distance” output).

Based on the “safe distance” output provided by the Carbdose calculator, ensure that the POET filters are placed in a safe area that avoids potential radiation to site users. Space limitations at sites may require that a protective barrier or shield be installed around the filter system to mitigate gamma radiation.

The GAC changeout schedule may need to be adjusted based on the “waste disposal” output provided by the Carbdose calculator. Even if breakthrough of petroleum compounds or bacteria buildup has not occurred, GAC filter media should be scheduled to be changed out prior to becoming low-level waste. The change out schedule may be so frequent that it is more cost effective to install a pre-treatment system for radon such as an aeration system.

Although the MEDEP’s purpose for analyzing a water supply for radon is to maintain GAC POET systems at homes, radon in water is considered a health risk independent of any potential risk caused by a petroleum discharge. DHHS suggests that radon treatment for health risk purposes should be considered for a water supply if the concentration in the well



water is greater than 4,000 pCi/L. If sample results are greater than 4,000 pCi/L, refer the homeowner to DHHS, Maine Radiation Control Program.

5.3.2 PROJECT SPECIFIC CONSIDERATIONS

For some Petroleum Program projects, GAC POET will remain installed as long-term mitigation of petroleum contamination in a water supply. In this case a long-term filter agreement is secured between the property owner and MEDEP. The MEDEP, Division of Resource Administration, Collections, Claims, and Recovery (CCR) Unit will assume monitoring of the water supply and POET system. The CCR Unit will need to be informed of how radon affects the GAC changeout schedule.

If site conditions and levels of petroleum contamination warrant that GAC filters are no longer needed at a site, then the filters should be removed and appropriately disposed. Occasionally, MEDEP staff leave GAC POET at sites even when it is not required for petroleum treatment. If the GAC filters are going to remain installed at a site, and not be maintained by the MEDEP (i.e. the concentrations of petroleum compounds in the water supply do not pose a health risk to the site user), a transfer of ownership agreement will need to be secured between the property owner and MEDEP. The transfer of ownership agreement should address the radon concentration and recommended changeout schedule if the radon concentration is greater than 4,000 pCi/L.

6. QUALITY ASSURANCE/QUALITY CONTROL

Data quality objectives (DQOs) should be stated in the SAP. Quality Assurance/Quality Control (QA/QC) samples may be collected if needed to meet DQOs. All analytical data should be reviewed and assessed to determine if DQOs have been met. If review indicates DQOs have not been met, corrective action will be recommended by the reviewer.

7. REFERENCES

<http://www.maine.gov/dhhs/mecdc/environmental-health/rad/radon/hp-radon.htm>



1. APPLICABILITY

This Standard Operating Procedure (SOP) applies at petroleum release sites where there is a large volume of petroleum released, *and* petroleum has reached, or is likely to reach the bedrock and/or groundwater.

This SOP applies to all programs in the Maine Department of Environmental Protection's (MEDEP) Bureau of Remediation and Waste Management (BRWM). It is also applicable to all parties that to all parties that investigate, mitigate, or remediate petroleum releases.

This SOP is not a rule and is not intended to have the force of law, nor does it create or affect any legal rights of any individual, all of which are determined by applicable statutes and law. This SOP does not supersede statutes or rules.

2. PURPOSE

The purpose of this document is to describe the MEDEP/BRWM procedure for determining if arsenic contamination of homeowner wells is attributable to biodegradation of petroleum hydrocarbons in ground water resulting in dissolution and desorption from ferric hydroxides. This document is intended to help MEDEP/BRWM staff determine when to be concerned that a water supply well is at risk of being contaminated with naturally-occurring arsenic that has been mobilized by biodegradation of petroleum hydrocarbons and what parameters to measure to evaluate this condition.

3. RESPONSIBILITIES

All MEDEP/BRWM Staff must follow this procedure when performing this task. All Managers and Supervisors are responsible for ensuring that their staff are familiar with and adhere to this procedure. MEDEP/BRWM staff reviewing data by outside parties are responsible for assuring that the procedure (or an equivalent) was utilized appropriately.

4. DEFINITIONS

- 4.1 ARSENIC CONTAMINATION – Detection of arsenic in groundwater or a water supply above the maximum contaminant level (MCL) of 10 micrograms per liter (ug/l).
- 4.2 BASELINE WATER QUALITY ANALYSIS: Groundwater or water supply analysis for arsenic, dissolved iron, dissolved manganese, pH, dissolved oxygen (DO), oxidation reduction potential (ORP), and specific conductance.
- 4.3 SECONDARY WATER QUALITY ANALYSIS: Groundwater or water supply analysis for major ions (calcium, sodium, magnesium, potassium, chlorine, sulfate, and nitrate), alkalinity, total organic carbon, and methane.



5. GUIDELINES AND PROCEDURES

5.1 INTRODUCTION

There are several factors that will control the release of arsenic to the groundwater at a petroleum spill including, but not limited to, the existence of a source of arsenic within the aquifer, the size of the spill, the length of time after the spill, and geologic conditions, such as the depth to bedrock or groundwater.

A small amount of petroleum product is capable of contaminating a nearby water supply well, but a large amount of petroleum product is necessary to drive the redox conditions of the aquifer to the point of iron reducing so that arsenic is mobilized. The amount that is necessary is dependent on the initial redox conditions, the amount of terminal electron acceptors, and the pathway of the petroleum to the groundwater. If the initial redox conditions are very oxidizing and there are abundant electron acceptors, it will take a larger volume of petroleum to feed the microbes required to reduce the electron acceptors. If there is a large volume of soil above the water table, this can store a lot of the petroleum which may not make it to the groundwater, and a larger volume of petroleum is required to influence the conditions of the aquifer. Furthermore, an evaluation on recent spills that are cleaned up quickly and where petroleum does not reach the bedrock groundwater showed that it is unlikely that reducing conditions will be incurred to the point of releasing arsenic to the groundwater.

The methodology presumes that the mechanism for mobilization is reductive dissolution and desorption from ferric hydroxide minerals in the aquifer and that the groundwater sampled retains evidence of the reducing chemical environment.

Arsenic contamination is here defined as a detection above the maximum contaminant level (MCL) of 10 micrograms per liter (ug/l). Elevated iron and manganese are taken as evidence of redox conditions that are reducing enough to mobilize iron, manganese, and arsenic. Iron will be considered elevated if it is measured above 5,000 ug/L, and manganese will be considered elevated if it is measured above 300 ug/l. Where the redox sensitive parameters result in an ambiguous indication of the redox state of the water, BRWM scientists will have to evaluate the weight of the evidence and use professional judgement.

5.2 PLANNING

A well-developed Conceptual Site Model (CSM) is imperative for effective use of this technique (RWM-PP-006). Prior to conducting any sampling event, a Sampling and Analysis Plan (SAP) should be developed (SOP RWM-PP-007). All water supply sampling should be conducted in accordance with MEDEP SOP RWM-PP-014.

5.3 PROCEDURE



5.3.1 OVERVIEW

BRWM staff should analyze for arsenic at sites where there is a large volume of petroleum released, *and* petroleum has reached, or is likely to reach, the bedrock and/or groundwater.

If it is determined that the water supply should be analyzed for arsenic, a Baseline Water Quality Analysis should be completed. At sites where the cause of high arsenic concentrations in a water supply well is not clear, a Secondary Water Quality Analysis including additional groundwater geochemistry parameters should be completed. The parameters to be included in the Baseline and Secondary Analyses are defined below.

Based on the spill scenarios and results of the Baseline Water Quality Analysis, there are several follow-up approaches to consider.

Analyzing for Arsenic Contamination at a Recent Spill

It generally takes a period of months for native microbes to acclimate to petroleum hydrocarbons as a food source and create the reducing conditions that can mobilize arsenic. If BRWM staff are certain that the spill was a discrete event and that it occurred within a few weeks prior to initial sampling, then a Baseline Water Quality Analysis sample may be collected to establish whether the water supply well had elevated arsenic before biodegradation of the petroleum began. Three possible outcomes of these analyses are evaluated below.

1. *The arsenic concentration is below the MCL, iron and manganese are not elevated, DO is greater than 1 milligram/liter (mg/l), and ORP is positive.* This indicates that the biodegradation of the petroleum hydrocarbons has not yet created reducing conditions in the aquifer, or there is insufficient arsenic in the aquifer.
 - a. Quarterly monitoring of pH, DO, ORP, and specific conductance should be completed.
 - b. The water supply well should be sampled for the Baseline Water Quality Analysis parameters at the end of quarterly sampling to determine if conditions have changed.
 - c. If redox conditions decrease and/or arsenic concentrations increase, this may be an indication that the petroleum has impacted water quality, and additional monitoring or a treatment system may be required.
2. *The arsenic concentration is below the MCL, iron and manganese are elevated, DO is less than 1 mg/l, and ORP is negative.* In this case, the water supply and aquifer already provide evidence of reducing conditions that enhance the mobility of arsenic, but there may not be sufficient arsenic in the aquifer materials to mobilize arsenic into the groundwater.
 - a. The water supply well should be sampled for the Baseline Water Quality Analysis parameters at the end of quarterly sampling.



- b. If arsenic concentrations are significantly greater than the initial Baseline Water Quality Analysis concentrations, this may be an indication that the petroleum has impacted water quality, and additional monitoring or a treatment system may be required.
3. *The arsenic concentration is above the MCL.* In this case, the water supply will be considered arsenic-contaminated prior to the petroleum discharge. The Department will not be responsible for providing water supply treatment unless the arsenic concentration subsequently increases so much in response to biodegradation of the petroleum that it subsequently increased the cost of appropriate point of use treatment.
 - a. Educate the well owner/operator about arsenic health impacts and treatment options and encourage them to address the issue.
 - b. The water supply well should be sampled for the Baseline Water Quality Analysis parameters at the end of quarterly sampling.
 - c. If arsenic concentrations are significantly greater than the initial Baseline Water Quality Analysis concentrations, this may be an indication that the petroleum has impacted water quality, and additional monitoring or a treatment system may be required.

Analyzing for Arsenic Contamination When the Date of the Release is Unknown

For those petroleum spills where a precise discharge date cannot be determined, and the site meets the criteria contained in the “When to Analyze Water Supply Wells for Arsenic” section of this guidance, collect a Baseline Water Quality Analysis sample upon detection of petroleum contamination in soil or groundwater. Four possible outcomes of these analyses are evaluated below.

1. *The arsenic concentration is below the MCL, iron and manganese are not elevated, DO is greater than 1 milligram/liter (mg/l), and ORP is positive.* This indicates that the biodegradation of the petroleum hydrocarbons has not yet created reducing conditions in the aquifer, or there is insufficient arsenic in the aquifer.
 - a. Quarterly monitoring of pH, DO, ORP, and specific conductance should be completed.
 - b. The water supply well should be sampled for the Baseline Water Quality Analysis parameters at the end of quarterly sampling to determine if conditions have changed.
 - c. If redox conditions decrease and/or arsenic concentrations increase, this may be an indication that the petroleum has impacted water quality, and additional monitoring or a treatment system may be required.
2. *The arsenic concentration is below the MCL, iron and manganese are elevated, DO is less than 1 mg/l, and ORP is negative.* In this case, the water supply and aquifer already provide evidence of reducing conditions that enhance the mobility of arsenic, but there may not be sufficient arsenic in the aquifer materials to mobilize arsenic into the groundwater.



- a. The water supply well should be sampled for the Baseline Water Quality Analysis parameters at the end of quarterly sampling.
 - b. If arsenic concentrations are significantly greater than the initial Baseline Water Quality Analysis concentrations, this may be an indication that the petroleum has impacted water quality, and additional monitoring or a treatment system may be required.
3. *The arsenic concentration is above the MCL, iron and manganese are not elevated, and the water contains dissolved oxygen greater than 1 mg/l and/or ORP is positive.* There is no evidence of reducing conditions capable of mobilizing arsenic, so the arsenic can be attributed to natural causes instead of the petroleum contamination. The assumption is that the system has reached equilibrium and no further reduction is occurring.
- a. Educate the well owner/operator about arsenic health impacts and treatment options and encourage them to address the issue.
4. *The arsenic concentration is above the MCL, iron and/or manganese are elevated, DO is less than 1 mg/l, and ORP is negative.* The water composition provides evidence of reductive dissolution of the ferric hydroxide minerals. The Department cannot prove that the arsenic was not mobilized by degradation of the petroleum, but it can obtain more data to assess the situation.
- a. The water supply well should be sampled for Secondary Water Quality Analysis parameters. This will help identify whether the water supply well is located in a recharge or discharge area. Wells located at the end of a flow path in a discharge zone typically have higher specific conductance, higher alkalinity, higher pH, higher sodium concentrations (but low chloride concentrations), as well as reducing conditions and are more likely to have naturally-occurring arsenic. If a well has a chemical signature typical of a recharge area (calcium carbonate-type water, low specific conductance, low pH, low alkalinity), but has reducing conditions, then it is more likely impacted by the presence of petroleum.

5.3.2 PROJECT SPECIFIC CONSIDERATIONS

At some sites where side- or up-gradient monitoring wells and water supply wells are available, it may be practical to evaluate background (side- or up-gradient) water quality to determine prevailing arsenic concentrations before the effects of the petroleum contamination. This type of study should include parameters contained in both the Baseline Water Quality Analysis and Secondary Water Quality Analysis so that the whole water chemistry of the contaminated water supplies can be compared to that of the side- or up-gradient monitoring points, not just the arsenic.

Great caution should be used when drawing conclusions based on neighboring wells. Investigations within Maine have shown that naturally-occurring arsenic concentrations



can vary significantly over short distances. A better approach would be to evaluate groundwater downgradient of the plume. If downgradient groundwater does not have high arsenic concentrations, then it is unlikely that the petroleum-contaminated site would.

6. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Any evaluation of background water quality that is the basis of decisions about water supply treatment must be thorough and convincing enough to withstand external peer review.

Data quality objectives (DQOs) should be stated in the SAP. Quality Assurance/Quality Control (QA/QC) samples may be collected if needed to meet DQOs. Typical types of QA/QC samples that may be collected or prepared at the laboratory include replicate matrix interference spike (MIS) samples to allow determination of an upper confidence limit (UCL) for the decision unit (DU), laboratory control blank spikes, and analysis of reference material containing known concentrations of the target analytes. All analytical data should be reviewed and assessed to determine if DQOs have been met. If review indicates DQOs have not been met, corrective action will be recommended by the reviewer.

7. REFERENCES

RWM-PP-006, Conceptual Site Model for Petroleum Contamination
RWM-PP-007, Development of a Sampling and Analysis Plan
RWM-PP-014, Water Sampling at Petroleum Sites

RWM-PP-014_WaterSamplingatPetroleumReleaseSites

Final Audit Report

2021-10-14

Created:	2021-08-30
By:	Lindsay Caron (LINDSAY.ER.CARON@MAINE.GOV)
Status:	Signed
Transaction ID:	CBJCHBCAABAABAH_EvTMDLiZpba0day16ZtIDbGIQJ9O2-

"RWM-PP-014_WaterSamplingatPetroleumReleaseSites" History

 Document created by Lindsay Caron (LINDSAY.ER.CARON@MAINE.GOV)

2021-08-30 - 2:41:36 AM GMT- IP address: 198.182.163.115

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2021-10-14 - 5:41:48 PM GMT- IP address: 104.47.64.254

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