

Protocol for the Contaminated Sites Regulation under the Environment Act

Protocol no. 5:

Petroleum hydrocarbon analytical methods and standards

Prepared pursuant to Part 6 – Administration, Section 21, Contaminated Sites Regulation, OIC 2002/171



Site-specific numerical standards

1. Introduction

Section 21(1)(c) of the Contaminated Sites Regulation, OIC 2002/171 (CSR) authorizes the Minister or his/her delegate to approve or adopt protocols for testing or analyzing soil, sediment, water, snow and other environmental media. This protocol has been adopted to clarify when and how the standards for various petroleum hydrocarbon (PHC) compounds must be applied.

Petroleum is a complex mixture of many hydrocarbon compounds. Some PHC compounds have been shown to have greater toxicity than others. When generic risk-based standards for petroleum hydrocarbons were first developed, they were initially prepared for these discrete compounds to ensure that human health and the environment were protected from the most significant risk. Once these standards were in place, "umbrella" standards, representing the summation of all PHC compounds within a certain carbon range, were developed to protect against the many additional compounds not covered by discrete standards. The CSR contains both umbrella standards and standards for a number of discrete PHCs.

2. CSR standards for petroleum hydrocarbons

In the CSR, there are two groups of discrete PHC standards and several umbrella standards.

The common, highly toxic PHC compounds with discrete CSR standards are:

- 2.1 Benzene, Toluene, Ethylbenzene, Xylene and Styrene. Collectively referred to as BTEX + Styrene (or sometimes more generally as MAH, monocyclic aromatic hydrocarbons), these five compounds are considered volatile, meaning that they have a relatively low boiling point and molecular weight.
- 2.2 Polycyclic Aromatic Hydrocarbons (PAH). PAH refers to hydrocarbon compounds containing two or more fused rings of carbon atoms, making them

heavier and less volatile than BTEX. Several PAHs, such as benzo[a]pyrene, naphthalene, phenanthrene and others, have specific standards in the CSR.

The umbrella parameters of PHC compounds with CSR standards are:

- 2.3 Volatile Petroleum Hydrocarbons in Soil (VPH) and in Water (VPH $_{\rm W}$). This group contains all petroleum hydrocarbons in the carbon range of C6-10, with the exception of BTEX + Styrene. BTEX + Styrene must be analyzed in order to calculate VPH or VPH $_{\rm W}$.
- 2.4 Volatile Hydrocarbons in Water (VH_{W6-10}). This group contains all petroleum hydrocarbons in the carbon range of C6-10, including BTEX + Styrene.
- 2.5 Light Extractable Petroleum Hydrocarbons in Soil (LEPH) and in Water (LEPH $_{\rm W}$). This group contains the PHCs with a carbon range of C10-19, with the exception of certain PAHs in the same weight range. PAHs must be analyzed in order to calculate LEPH or LEPH $_{\rm W}$.
- 2.6 Extractable Petroleum Hydrocarbons in Water, C10-19 (EPH $_{W10-19}$). This group contains all petroleum hydrocarbons in the carbon range of C10-19, including applicable PAHs.
- 2.7 Heavy Extractable Petroleum Hydrocarbons in Soil (HEPH). This group contains the PHCs with a carbon range of C19-32, with the exception of certain PAHs in the same carbon range. PAHs must be analyzed in order to calculate HEPH.

In addition, three umbrella parameters, for which there are no CSR standards, are often used by consultants as interim or preliminary indicators of contaminant levels in soil:

- 2.8 Volatile Hydrocarbons in Soil (VH $_{S6-10}$). This group contains all petroleum hydrocarbons in the carbon range of C6-10, including BTEX + Styrene, but the distinct concentrations of BTEX + Styrene cannot be calculated. There is no standard for VH $_{S6-10}$ in the CSR; the regulated standard is VPH.
- 2.9 Extractable Petroleum Hydrocarbons in Soil, C10-19 (EPH $_{\rm S10-19}$). This group contains all petroleum hydrocarbons in the carbon range of C10-19, including applicable PAHs, but the distinct concentrations of PAHs cannot be calculated. There is no standard for EPH $_{\rm S10-19}$ in the CSR; the regulated standard is LEPH.
- 2.10 Extractable Petroleum Hydrocarbons in Soil, C19-32 (EPH $_{\rm S19-32}$). This group contains all petroleum hydrocarbons in the carbon range of C19-32, including applicable PAHs, but the distinct concentrations of PAHs cannot be calculated. There is no standard for EPH $_{\rm S19-32}$ in the CSR; the regulated standard is HEPH.

BTEX + Styrene and PAHs should always be of concern when assessing or remediating contaminated sites. Discrete standards were developed for these compounds because they can pose the greatest risk to human health and the environment due to their toxic natures. Analyzing BTEX + Styrene and PAHs to calculate VPH, LEPH, and HEPH is associated with higher laboratory analysis costs than the less expensive corresponding non-regulated parameters of VH_{S6-10}, EPH_{S10-19}, and EPH_{S19-32}. However, it is important that the concentrations of BTEX + Styrene and PAH be characterized in accordance with this protocol to ensure that these compounds are not present in unsafe quantities. Failure to do so may result in the rejection of data as incomplete, and the potential determination of the site as contaminated under the CSR.

For more information on the analytes described in this section and their associated laboratory methods, please contact the Standards & Approvals section of the Environmental Programs Branch, or consult the website of the British Columbia Ministry of Environment:

https://www2.gov.bc.ca/gov/content/environment/air-land-water/site-remediation/guidance-resources/analytical-methods.

3. Use of CSR soil standards at petroleum-impacted sites

In general, analysis of soil samples taken from sites contaminated with petroleum hydrocarbons $\underline{\text{must}}$ be undertaken for the parameters VPH, LEPH, and HEPH, as well as BTEX + Styrene and all regulated PAHs. Under the specific circumstances outlined below, VH_{S6-10}, EPH_{S10-19}, and EPH_{S19-32} can be compared to the CSR standards for VPH, LEPH, and HEPH.

- 3.1 When **characterizing contaminated material**, at least the first five samples for each contaminant plume must be analyzed for BTEX + Styrene and PAHs. If more than five samples are taken from a single plume, the remainder can be analyzed only for VH_{S6-10}, EPH_{S10-19}, and EPH_{S19-32}. The samples analyzed for BTEX + Styrene and PAHs should be taken from the area thought to be the most contaminated.
- 3.2 When **conducting confirmatory sampling** at large sites, at least the first five confirmatory samples for each contaminant plume at any site must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and all regulated PAHs. After that, only

every tenth confirmatory sample needs this analysis; the remainder can be analyzed for VH $_{S6-10}$, EPH $_{S10-19}$, and EPH $_{S19-32}$. For example, in addition to samples #1 through #5, sample #10, sample #20, etc. will also require analysis of all regulated hydrocarbon parameters. If all samples taken when characterizing contaminated material as described in section 3.1 above show that all BTEX + Styrene and PAH concentrations are below their respective applicable CSR standards, BTEX + Styrene and PAH analysis is not required for any confirmatory samples.

- 3.3 When **conducting interim sampling** for the purpose of assessing the rate of remediation of soil being treated at a land treatment facility, BTEX + Styrene and PAH need not be analyzed; VH_{S6-10} , EPH_{S10-19} , and EPH_{S19-32} may be used.
- 3.4 When sampling to demonstrate that remediated soil is ready to be removed from a land treatment facility, VPH, LEPH, HEPH, BTEX + Styrene, and all regulated PAHs must be tested for the first five samples of soil from each source, except where previous sampling and analysis performed in accordance with section 3.1 above has demonstrated that a particular contaminant does not exceed the applicable CSR standard. After those first five samples, only every tenth sample needs this analysis (beginning with sample #10); the remainder can be sampled for only VH_{S6-10}, EPH_{S10-19}, and EPH_{S19-32}. See also Protocol 11: Sampling Procedures for Land Treatment Facilities.

Other compounds with discrete standards, such as halogenated hydrocarbons, may be present in fuel in minute quantities, but these need not be analyzed except at sites where they are suspected to be contaminants of concern.

Please refer to Protocol No. 3: Soil Sampling Procedures at Contaminated Sites for further information regarding sampling rate requirements at contaminated sites.

4. Use of VH and EPH analysis at petroleum-impacted sites

In accordance with section 3.0 above, it is in some cases acceptable to analyze soil samples for VH $_{S6-10}$, EPH $_{S10-19}$, and EPH $_{S19-32}$ instead of the regulated parameters VPH, LEPH, and HEPH. Under these circumstances, Environment Yukon may compare the VH $_{S6-10}$, EPH $_{S10-19}$, and EPH $_{S19-32}$ analytical results directly to the corresponding CSR standard (VPH, LEPH, and HEPH, respectively) for the purpose of determining whether or not a site is contaminated.

At historical sites where previous assessment activities do not conform to current-day CSR protocols and VPH, LEPH, and HEPH results are not available, Environment Yukon may use VH_{S6-10}, EPH_{S10-19}, and EPH_{S19-32} results to determine if a site is contaminated.

The comparison of VH_{S6-10} , EPH_{S10-19} , and EPH_{S19-32} analytical results to the corresponding CSR parameter as described herein does not negate the need to analyze a sufficient number of soil samples for all contaminants of concern, including BTEX + Styrene and PAHs as described in section 3.0 of this protocol

5. Use of the Canada-wide standards at petroleumimpacted sites

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) is a relatively new standard for assessing petroleum hydrocarbon contamination. The Yukon is a signatory to this standard and has proposed to adopt it when the CSR is next amended. However, until the regulation is amended, analyses using the parameters specified in the PHC CWS cannot be used to demonstrate compliance with the CSR standards.

For more information on the Canada-Wide Standard and its application in the Yukon, please contact the Standards & Approvals section. The standard itself is available on the website of the Canadian Council of Ministers of the Environment:

http://www.ccme.ca/ourwork/soil.html?category_id=43

6. Use of CSR water standards and petroleum-impacted sites

As the PHC CWS is only a soil standard, the applicable water standards will not change with the adoption of the CWS. When dealing with water samples, the CSR standards for VH_{W6-10} and EPH_{W10-19} apply at all sites, and all samples must be analyzed for these parameters. In addition:

- a. When aquatic life water standards apply, samples must be analyzed for VPH_W, LEPH_W, benzene, ethylbenzene, styrene, toluene and all regulated PAHs.\
- b. When drinking water standards apply, samples must be analyzed for BTEX and the PAH benzo[a]pyrene

7. Examples

The following examples demonstrate the principles discussed above. In the first scenario, a spill site is assessed and remediated in a single stage with no opportunity to review sample results before completing the work. The second scenario discusses the remediation of a large site with three contaminant plumes for which previous samples are available.

7.1 Spill response: combined assessment and remediation

Situation: a tanker truck carrying diesel fuel flips over into a ditch beside a highway and starts leaking. A river crosses the highway about 100 m away from the crash site. The spill is contained, and equipment is immediately mobilized to excavate the contaminated soil, in the amount of approximately 2000 cubic metres. In accordance with Protocol 3: Soil Sampling Procedures for Contaminated Sites, the excavated contaminated material is sampled at a rate of one sample for every 50 cubic metres for a total of 40 samples. As soon as the contaminated material is removed, 30 confirmatory samples are taken from the base and walls of the excavation. Groundwater has been slowly infiltrating into the excavation; as a precaution due to the close proximity of the river, a monitoring well is installed downgradient of the spill site and one groundwater sample is taken. The excavated material is bioremediated at a land treatment facility; after one year, the facility operator takes 10 interim samples to assess the rate of remediation, and after two years, he takes one confirmatory sample for every 100 cubic metres of material for a total of 20 samples (as required by Protocol 11: Sampling Procedures for Land Treatment Facilities) to verify that treatment is complete.

The following analyses must be undertaken:

a. At least five samples of the excavated contaminated soil must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and PAHs. Since the contamination is all from a single source, the remaining 35 samples may, if desired, be analyzed for only VH_{S6-10} , EPH_{S10-19} , and EPH_{S19-32} to reduce laboratory costs.

- b. Since the analytical results for the characterization samples will not yet be available, the first five confirmatory samples taken from the excavation and every tenth confirmatory sample thereafter (for a total of 8 out of the 30 samples collected) must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and PAHs. The other 22 confirmatory samples may, if desired, be analyzed for only VH_{S6-10} , EPH_{S10-19} , and EPH_{S19-32} to reduce laboratory costs.
- c. Because the aquatic life standards apply at the site (surface water is within 1 km), the groundwater sample must be analyzed for VH_{W6-10} , EPH_{W10-19} , VPH_{W} , $LEPH_{W}$, BTEX + Styrene, and PAHs.
- d. The 10 interim samples taken from the land treatment facility to assess the rate of remediation (i.e. those taken after the first year of remediation) may be analyzed using whichever parameters the facility operator prefers. It is common to analyze such samples for VH_{S6-10} , EPH_{S10-19} , and EPH_{S19-32} .
- e. The first five confirmatory samples taken from the land treatment facility to verify that remediation is complete, and every tenth confirmatory sample thereafter (for a total of 7 out of the 20 samples collected), must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and PAHs. The other 13 confirmatory samples may, if desired, be analyzed for only VH $_{S6-10}$, EPH $_{S10-19}$, and EPH $_{S19-32}$ to reduce laboratory costs. (For clarify, if characterization sampling showed BTEX + Styrene and PAHs above CSR standards and interim analysis only analyzed for VH $_{S6-10}$, EPH $_{S10-19}$, and EPH $_{S19-32}$, then the 7 samples taken for the purpose of verifying remediation must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and PAHs.)

7.2 Large site with multiple contaminant plumes

Situation: A large industrial site is being decommissioned and sold. Previous uses of the site included fuel handling and storage of creosote-treated wood. Following a comprehensive drilling program, three distinct contaminant plumes are identified: one below a tank used for diesel fuel for vehicles, a second below a tank used for heating fuel, and a third in the treated wood storage area. Because the three plumes originated from different sources, they must be assessed separately.

7.2.1 Plume #1: BTEX and PAHs not detectable

During the drilling program, the volume of contaminated material in the first plume is estimated at 200 m³. As required by Protocol 3: Soil Sampling Procedures for Contaminated Sites, four samples are taken from the boreholes to characterize the contaminated material. The results of these samples show that BTEX + Styrene and PAHs are not present in detectable concentrations. The contaminated material is then excavated and removed to a permitted treatment facility, and eight confirmatory samples are taken from the base and walls of the excavation to ensure that all contamination has been removed.

The following analyses must be undertaken:

- a. All four borehole samples of contaminated soil must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and PAHs.
- b. All eight confirmatory samples taken from the excavation may be analyzed for only VH_{S6-10} , EPH_{S10-19} , and EPH_{19-32} , since BTEX + Styrene and PAHs were below CSR standards in the characterization samples.

7.2.2 Plume #2: PAHs detectable but below applicable standards

During the drilling program, the volume of contaminated material in the second plume is estimated at 400 m³. As required by Protocol 3: Soil Sampling Procedures for Contaminated Sites, eight samples are taken from the boreholes to characterize the contaminated material. The results of these samples show that BTEX + Styrene and PAHs are present, but that the concentrations of these substances are below the standards for industrial land use in the Contaminated Sites Regulation. The contaminated material is then excavated and removed to a permitted treatment facility, and 14 confirmatory samples are taken from the base and walls of the excavation to ensure that all contamination has been removed.

The following analyses must be undertaken:

- a. Five of the eight borehole samples of excavated contaminated soil must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and PAHs. The remaining three samples may be analyzed for only VH_{S6-10} , EPH_{S10-19} , and EPH_{S19-32} .
- b. Since BTEX + Styrene and PAHs were detected in the characterization samples, but were below CSR standards, the confirmatory samples taken from the excavation may be analyzed for only VH_{S6-10} , EPH_{S10-19} , and EPH_{S19-32} to reduce laboratory costs, if desired.

7.2.3 Plume #3: PAHs present above applicable standards

During the drilling program, the volume of contaminated material in the third plume is estimated at 100 m³. As required by Protocol 3: Soil Sampling Procedures for Contaminated Sites, two samples are taken from the boreholes to characterize the contaminated material. The results of these samples show that BTEX + Styrene are not present in detectable concentrations, but that several PAH concentrations are above the standards for industrial land use in the Contaminated Sites Regulation. The contaminated material is then excavated and removed to a permitted treatment facility, and five confirmatory samples are taken from the base and walls of the excavation to ensure that all contamination has been removed.

The following analyses must be undertaken:

- a. Both of the two borehole samples of excavated contaminated soil must be analyzed for VPH, LEPH, HEPH, BTEX + Styrene, and PAHs.
- b. All five confirmatory samples taken from the excavation must be analyzed for VH_{6-10} , LEPH, HEPH, and PAHs, since PAHs were detected in the characterization samples. BTEX + Styrene need not be analyzed since they were not detected in the characterization samples.

8. Effective date

The effective date of this protocol shall be December 20, 2017 and it shall remain in effect until replaced or rescinded by the Standards & Approvals section.

9. Failure to comply

When sample analysis fails to meet the requirements of this protocol after its effective date, the proponent will be required to take new samples to satisfy those requirements. This may include, for example, re-sampling contaminated material that has been taken to a land treatment facility or re-excavating the originating site to take new confirmatory samples.

10. Additional information

For more information about contaminated sites, please contact:

Email: envprot@gov.yk.ca

Phone: 867-667-5683 or toll free in Yukon: 1-800-661-0408, ext. 5683.

Approved:

Date: December 20, 2017

Manager, Standards and Approvals Section

Environmental Protection and Assessment Branch

Department of Environment