APPENDIX C

Montana Method – Analytical Analyses

Montana Method for Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH)

The Montana Method is based on the Massachusetts Department of Environmental Protection (MADEP) Method for the Determination of Volatile Petroleum Hydrocarbons (MADEP February 2018 Revision 2.1 (PID/FID); and the GS/MS option MADEP January 2017 Revision 0) and The Method for the Determination of Extractable Petroleum Hydrocarbons Extractable Petroleum Hydrocarbons (MADEP December 2019 Revision 2.1.

1.0 Montana Volatile Petroleum Hydrocarbons Method

The Montana Volatile Petroleum Hydrocarbons (VPH) Method adopts the Massachusetts VPH Method but with the following modifications and/or clarifications:

2.0 Sample Preservation and Holding Times

2.1 Soil/Sediment Samples

Soil/sediment samples may be collected in 4 oz. (120mL) wide mouth glass jars or 60 mL/40 mL VOA vials with Teflon-lined screw caps. Soil/sediment samples must be preserved in methanol as described in the Massachusetts VPH Method. Samples can be collected in the field with pre-preserved jars or sent to the laboratory to preserve within 48 hours of sample collection.

Pre-preserved collection method: The pre-preserved jars will be pre-weighed with the measured volume of methanol clearly marked. Most labs will provide a load sampling device with a handle portion and a syringe to collect the sample. Measurements will be clearly marked on the handle in grams. The desired ratio is 1g:1mL methanol or for 25 mL methanol add soil until the meniscus of the methanol is approximately at the 40 mL line; for 15 mL of methanol, add to approximately the 25 mL line. In all cases, the level of soil in the container may not rise above the level of methanol. If any methanol is lost during sampling from a spill, splash, etc. it must be discarded and redone.

Airtight field collection, methanol added in lab method: When collecting a sample without methanol, samplers/containers must allow for the collection and airtight storage of at least 5-25 grams of soil (airtight collection samplers that many labs will provide, or a 30 ml plastic syringe with the end sliced off is recommended). Documentation must be provided to ensure an airtight seal of the sampler/container (record sampling technique and containers used). All soil/sediment samples must be immediately cooled and maintained at a temperature of 4°C $^{+}$2°C. Samples must be extruded and immersed in methanol at the laboratory within 48 hours of sampling. Soil/sediment samples must be analyzed within 28 days of sample extraction.

Moisture Analysis: For both methods of soil sampling described above, a sample containing no methanol must also be submitted for determining moisture percentage. This sample does not need to be collected in a sealed sampler/container.

2.2 Aqueous Samples

Aqueous samples should be collected in 40-ml glass volatile organic analyte (VOC) vials with Teflon lined septa screw caps. Samples must have zero headspace remaining when filled and must be acidified to pH of 2.0 or less at the time of collection. The pH can be adjusted to the appropriate level by adding 3 or 4 (up to 10 drops HCl may be added) drops of 1:1 HCl to each 40-ml sample vial prior to collection. All aqueous samples must be immediately cooled and

maintained at a temperature of 4°C ±2°C immediately after collection. Aqueous samples must be analyzed within 14 days of sample collection.

If the sample can be analyzed within 4 hours, HCl preservation is not necessary. If the sample effervesces, analysis of an un-preserved sample is recommended if the lab can accommodate the 4-hour timeframe.

Acid preservation is useful for the analysis of most VOCs and petroleum hydrocarbons, but significant losses can occur for ethers, such as MTBE. The combination of low pH and high temperatures dramatically increases the likelihood of hydrolysis. Therefore, with acid preservation, a heated purge method is not allowed for this method. If a heated purge is necessary to achieve proper analyte purge/partitioning, the sample could be preserved to a pH of greater than 11.0 using trisodium phosphate dodecahydrate and a heated purge. This is described in the method and is considered a significant modification of the method. A significant modification means there is no assured certainty of results obtained under these conditions.

3.0 Reporting

Moisture content of soil/sediment samples must be reported, and analytical results are to be reported on a dry-weight basis.

For comparison to Risk Based Screening Levels (RBSL), the concentrations of VPH fractions in soil/sediment and aqueous samples are adjusted to remove target compound concentrations that are specifically reported (e.g., benzene, toluene, etc.). VPH fractions include: C5-C8 aliphatics, C9-C12 aliphatics, and C9-C10 aromatics. C5-C8 aliphatics value is corrected for quantified analytes, such as MTBE, benzene and toluene, which have their own screening levels or standards. C9-C12 aliphatics value is corrected for target VPH analytes that are quantified and elute in this range, such as ethylbenzene, m, p, & o- xylenes and C9-C10 aromatics. No adjustments are made to the C9-C10 aromatics.

In addition to the target analytes and hydrocarbon fractions, laboratories must generate a Total Purgeable Hydrocarbons (TPH) result for soil/sediment and aqueous samples. The TPH value should include all Flame Ionization Detector (FID) hydrocarbon response, regardless of elution time. Quantify the response using the FID average response factor for all the VPH calibration mix constituents (do not include surrogates).

Analytical data packages should include a summary report that cross references the sample identification with the laboratory identification and identifies variations from standard operating procedures; laboratory analytical results; quality control data, which may include but is not limited to: surrogate recoveries, initial and continuing calibration blanks and spikes, method blanks, laboratory control blanks and spikes, and matrix spike and matrix spike duplicates; FID and photoionization (PID) chromatograms; chain of custody form(s); and a sample receipt checklist.

4.0 Montana Extractable Petroleum Hydrocarbons Method

The Montana EPH Method adopts the Massachusetts EPH Method with the following modifications and/or clarifications.

4.1 Sample Preservation and Holding Times

4.1.1 Soil/Sediment Samples

Soil/sediment samples are collected in 4 oz. (120 mL) wide-mouth amber glass jars with Teflon-lined screw caps. All soil/sediment samples must be immediately cooled and maintained at a temperature of 4°C $^{\pm}$2°C. Soil/sediment samples must be extracted by the laboratory within 14 days of sample collection and must be analyzed within 40 days of sample extraction.

4.1.2 Aqueous Samples

Aqueous samples should be collected in 1-liter amber glass bottles with Teflon lined screw caps. Samples must be preserved at the time of sampling by adding a suitable acid to reduce the pH to less than 2.0. The pH can be adjusted to the appropriate level by adding 5 ml of 1:1 HCl or other suitable acid to each bottle. All aqueous samples must be immediately cooled and maintained at a temperature of 4°C $^{\pm}$2°C immediately after collection. Aqueous samples must be extracted within 14 days of sample collection and analyzed within 40 days.

4.2 EPH Screen

The EPH method can be broken down into a two-step process. The first step, referred to as an EPH screen, is an extraction and analysis of hydrocarbons from the sample that generates a total extractable hydrocarbon (TEH) value. While the EPH screen provides little information on the chemical constituents, environmental fate of petroleum mixtures or toxicity it can be a cost-effective screening tool when relatively low concentrations of contamination are suspected. The laboratory determines the TEH number by determining the total area count for all peaks eluting in the C9-C36 aliphatic hydrocarbon range (this range includes the aromatic hydrocarbons as well). The lab will determine the peak area count for the surrogate compounds and subtract this area from the total area count. The TEH screen concentration is then quantified using the average response factor for all FID calibrated compounds (or MS). Further, fractionation and analysis is not required for samples that do not exceed the trigger value. The screening step may be omitted for samples that, based upon appearance and/or odor, or previous sample results, will exceed the trigger value.

To determine the fractions (C9-C18, C19-C36 aliphatics and C11-C22 aromatics), the sample is run through a silica gel column and analyzed as described in the method.
Some laboratories also report a post-silica gel TEH (or post-fractionated TEH). Running the sample that generates the TEH through a silica gel column (fractionation), results in the following two samples: aromatic and aliphatic hydrocarbons. The total area count for all peaks eluting in the C9-C36 aliphatic hydrocarbon range for the aliphatic fraction and the total area count for all peaks eluting in the C11 through C22 hydrocarbon range for the aromatic fraction (minus surrogate compounds) are added together to give the post-fractionated TEH. Though this number is not used for screening or regulatory purposes, it may be helpful to understand how much non-hydrocarbon mass has been removed. Non-hydrocarbon could include polar breakdown products of hydrocarbons, naturally occurring organic matter or other non-petroleum organics.

4.2.1 Soil/Sediment Samples

Soil/sediment sample with results that exceed trigger value of 200 mg/kg require the silica gel cleanup and EPH fractionation step to determine the aliphatic (C9-C18 aliphatics and C19-C36 aliphatics) and aromatic (C11-C22 aromatics) fractions.

4.2.2 Aqueous Samples

Groundwater samples reporting TEH concentrations at or above the trigger value of 1,000 µg/L require fractionation. If the sample is fractionated, labs are required to report the EPH screen concentration, the C9-C18 aliphatics, C19-C36 aliphatics, C11-C22 aromatic fraction concentrations, along with the post-fractionation TEH concentration.

4.2.3 Reporting

The C11-C22 aromatic fractions are adjusted for target compounds only when the combined target PAH concentration (total concentration of the 13 PAH target compounds) is three percent or greater of the C11-C22 aromatic concentration. The C11-C22 aromatic adjustment is accomplished by subtracting the combined target PAH concentrations from the C11-C22 aromatic fractions concentration.

Analytical data packages should include a summary report that cross references the sample identification with the laboratory identification and identifies variations from standard operating procedures; laboratory analytical results; quality control data, which may include but is not limited to: surrogate recoveries, initial and continuing calibration blanks and spikes, method blanks, laboratory control blanks and spikes, and matrix spike and matrix spike duplicates; FID chromatograms; chain of custody form(s); and a sample receipt checklist. [Note that other programs may have differing lists of what is required in an analytical data package, so check with the specific program regulating the release for more details.] Please see the Montana Quality Assurance Plan for Investigation of Underground Storage Tank Releases for more information on reporting requirements (DEQ, 2022; https://deq.mt.gov/files/Land/LUST/Documents/downloadables/QAPP-March2022_draft.pdf).