

# **Appendix C**

## **MONTANA METHOD**

## **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 May 2004, Revision 1.1) and The Method for the Determination of Extractable Petroleum Hydrocarbons Extractable Petroleum Hydrocarbons (MADEP May 2004, Revision 1.1).

### **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:

#### **Sample Preservation and Holding Times**

##### **Soil/Sediment Samples**

Soil/sediment samples may be collected in 4 oz. (120 mL) wide-mouth glass jars with Teflon-lined screw caps. Soil/sediment samples may be preserved in the field with methanol as described in the Massachusetts VPH Method, however it is not required at this time. All soil/sediment samples must be immediately cooled and maintained at a temperature of  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . Soil/sediment samples must be extracted by the laboratory within 7 days of sample collection and must be analyzed within 28 days of sample extraction.

If soil/sediment samples are preserved in the field with methanol, a sample containing no methanol must also be submitted for determining moisture percentage. Otherwise, soil moisture can be obtained from the same 4 oz. sample jar used for collecting the soil/sediment sample submitted for VPH analysis.

##### **Aqueous Samples**

Aqueous samples should be collected in 40-ml glass volatile organic analyte (VOA) 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. All aqueous samples must be immediately cooled and maintained at a temperature of  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  immediately after collection. Aqueous samples must be analyzed within 14 days of sample collection.

If groundwater conditions are such that the addition of acid preservative causes the sample to effervesce, the sample may be submitted without a field pH adjustment. The aqueous sample must be immediately cooled and maintained at a temperature of  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  immediately after collection. Aqueous samples without a field pH adjustment must be analyzed within 7 days of sample collection.

#### **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 target aromatic compounds benzene and toluene. C9-C12 aliphatics value is corrected for aromatic target compounds 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) results 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 of 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.

### **Second Column or Second Method Confirmation of MTBE and Naphthalene**

DEQ is requiring a second column or second method confirmation of naphthalene and MTBE for soil/sediment and groundwater samples if concentrations of MTBE or naphthalene (reported via VPH analyses) are greater than one-half of the default RBCA Tier 1 RBSLs. Additional compounds elute at approximately the same times as naphthalene and MTBE, making it difficult for analysts to distinguish the target compounds from non-target compounds. Second column confirmation will aid in identifying the target compounds.

MTBE was legislatively banned in Montana in 2005. MTBE should be analyzed at any gasoline release that could have begun before 2005. Gasoline releases that are known to have started after the 2005 Montana MTBE ban do not need to sample for MTBE unless other circumstances are believed to exist. Second column confirmation may be warranted at sites on a case by case basis where MTBE has been reported at low concentrations and determining its presence or absence is important in evaluating the source of the contamination. Work directly with your DEQ technical contact for site-specific requirements.

## **Montana Extractable Petroleum Hydrocarbons Method**

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

### **Sample Preservation and Holding Times**

#### **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 ±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.

#### **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 ±2°C immediately after collection. Aqueous samples must be extracted within 14 days of sample collection and analyzed within 40 days.

### **Screening Level**

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. The TEH number should include all FID hydrocarbon response regardless of elution time. Quantify the screening concentration using the average response factor for all FID calibrated EPH aliphatic constituents (do not include surrogates). Further fractionation and analysis is not required for samples that do not exceed the screening limit. The screening step may be omitted for samples that, based upon appearance and/or odor, will exceed the screening limit.

#### **Soil/Sediment Samples**

Soil/sediment sample with results that exceed screening limit of 200 parts per million (ppm) 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.

#### **Aqueous Samples**

Groundwater samples reporting TEH concentrations at or above the screening limit of 1,000 parts per billion (ppb) 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.

### **PAH analysis**

The necessity of the PAH analysis for soil/sediment and aqueous samples will be determined on a case by case basis by the DEQ technical contact. With the exception of naphthalene, which in

included in VPH analyses, PAHs are typically not found in diesel or jet fuel. A release of waste oil, heavy-end hydrocarbons such as Bunker C, and/or unknown wastes should be analyzed for PAHs. The requisite sampling parameters will be supplied to the lab by the case manager prior to submitting the samples to the lab. Work with your DEQ technical contact for advice on how to proceed.

PAHs are to be analyzed using EPA Method 8270C or 8270D. 1-Methylnaphthalene and 2-methylnaphthalene were added to the 13 target PAHs listed in the 2009 version of RBCA. The concentrations of 1-methylnaphthalene and 2-methylnaphthalene, plus the other 13 target PAHs, are only subtracted from the C11-C22 aromatic fractions when the combined PAH concentration is three percent of the C11-C22 aromatic concentration or greater.

### **Reporting:**

The C11-C22 aromatic fractions are adjusted for target compounds only when the combined target PAH concentration 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.