State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Extractable Petroleum Hydrocarbons

by the

Massachusetts DEP EPH Method

Version 3.0

Month 2023

Written by the Connecticut DEEP QA/QC Workgroup

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ACRONYM LIST

ACRONYM	DEFINITION
APS	Additional Polluting Substances
CASN	Chemical Abstracts Service Number
CCV	Continuing calibration verification
COD	Chloro-octadecane
%D	Percent difference or percent drift
DEEP	CT Department of Energy and Environmental Protection
DF	Dilution factor
EP	Environmental Professional
EPH	Extractable Petroleum Hydrocarbons
FID	Flame Ionization Detection
g	grams
GC	Gas chromatograph
GC/MS	Gas chromatography/mass spectrometry
HCl	Hydrochloric acid
ICV	Initial calibration verification
LCS	Laboratory control sample
LCSD	Laboratory control sample duplicate
LLOQ	Lower Limit of Quantitation
mL	Milliliters
MS	Matrix spike
MSD	Matrix spike duplicate
MSE	Microscale solvent extraction
NA	Not applicable
NAPL	Non-aqueous phase liquid
OHM	Oil and Hazardous Materials
OTP	Ortho-terphenyl
PAH	Polynuclear Aromatic Hydrocarbon
PFE	Pressurized fluid extraction
QA	Quality assurance
QC	Quality control
r/r^2	Correlation coefficient
%R	Percent recovery
%RSD	Percent relative standard deviation
RCP	Reasonable Confidence Protocol
RL	Reporting limit
RPD	Relative percent difference
RSR/RSRs	Remediation Standard Regulations
SIM	Selective ion monitoring
SPE	Solid phase extraction
TPH	Total petroleum hydrocarbons
UCM	Unresolved complex mixture
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µL	microliters

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1.0 Quality Assurance and Quality Control Requirements for MassDEP EPH Method

1.1 Method Overview

The Extractable Petroleum Hydrocarbons ("EPH") Method ("the EPH Method") is based on a solvent extraction, silica gel solid-phase extraction ("SPE")/fractionation process and gas chromatography ("GC") analysis using a flame ionization detector ("FID") to identify and quantify both Target Polynuclear Aromatic Hydrocarbons ("PAH") analytes and method-defined aliphatic and aromatic hydrocarbon fractional ranges in water, soils and sediments. Extractable aliphatic hydrocarbons are collectively quantified within two specific ranges: C_9 through C_{18}, and C_{19} through C_{36}. Extractable aromatic hydrocarbons are collectively quantified within the C_{11} through C_{22} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150°C and 265°C. This method may also be used to identify and quantify specific Target PAH Analytes, including Diesel PAH analytes.

All references to SW-846 Methods (i.e., SW-846 8000, 8270, etc.) in this document refer to the United States Environmental Protection Agency's most recently published version. All references to "the EPH Method" in this document refer to latest promulgated version of the MassDEP EPH Method.

The EPH Method is designed to complement and support the toxicological approach developed by the Connecticut Department of Energy and Environmental Protection ("DEEP") to evaluate human health hazards that may result from exposure to petroleum hydrocarbons. It is intended to produce data in a format suitable for evaluation by that approach.

Overall usability of data produced using this RCP protocol should be evaluated for compliance with project-specific data quality objectives, regardless of "Presumptive Certainty" status.

Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuels, and certain petroleum-based lubricating oils. The EPH Method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products, that contain lower or higher boiling components or distillates of aliphatic and/or aromatic hydrocarbons that are outside the aforementioned analytical range (C_9 through C_{36} aliphatic and aromatic ranges) of the EPH Method.

1.2 Summary of the EPH Method

This method is suitable for the analysis of waters, soils, sediments and non-aqueous phase liquids ("NAPL") after appropriate sample concentration and cleanup. A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish apparatus. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using commercially available silica gel cartridges or self-packed silica gel columns. The extracts are then separately analyzed by a capillary column GC equipped with a narrow- or wide-bore fused silica capillary column. The GC oven is temperature-programmed to facilitate separation of the analytes of interest, which are then detected by an FID that is interfaced directly to the GC. The resultant chromatogram of aliphatic compounds is collectively integrated within the C_9 through C_{18} and C_{19} through C_{36} ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C_{11} through C_{22} range and is (optionally) used to identify and quantify individual concentrations of Diesel and/or other Target PAH Analytes. It should be noted that the chromatogram resulting from the analysis of an extract which has not been fractionated is collectively integrated within the C_9 through C_{36} range to provide the concentration of TPH. Identification of Target PAH Analytes is accomplished by comparing the retention time of the PAH in the sample with the retention time of the PAH in standards obtained under identical analytical conditions.

Average calibration factors, or response factors, determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbons.

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An average calibration factor or response factor determined using a PAH standard mixture is used to calculate a collective C_{11} through C_{22} aromatic hydrocarbon concentration. Calibration factors or response factors determined for individual components of the PAH standard mixture are also used to calculate individual concentrations of Diesel and Target PAH Analytes. The EPH Method marker compounds and retention time windows are summarized in Table 1.0.

Table 1.0: EPH Method Marker Compounds

Range/Hydrocarbon Marker	Beginning Marker Compound	Ending Marker Compound
C_9 - C_{18} Aliphatic Hydrocarbons	0.1 Minutes before n-Nonane	0.1 Minutes before n-Nonadecane
C_{19} - C_{36} Aliphatic Hydrocarbons	0.1 Minutes before n-Nonadecane	0.1 Minutes after n-Hexatriacontane
C_{11} - C_{22} Aromatic Hydrocarbons	0.1 Minutes before Naphthalene	0.1 Minutes after Benzo(g,h,i)perylene

1.2.1 Sample Analysis Procedure

The analytical procedure for both water and solid samples are described in detail in the EPH Method. Approved matrix-specific extraction procedures are also described in the EPH method and are presented in Table 2.0 below. In general, a measured volume or weight of sample, 1 L for liquids and 10 grams for solids, is extracted using the appropriate matrix-specific sample extraction technique. Samples are first extracted with methylene chloride, and then solvent exchanged into hexane. Alternative extraction procedures other than those listed in Table 2.0 are acceptable, provided that the laboratory can document acceptable performance. However, use of an alternative extraction procedure is considered a "significant modification" of the EPH method pursuant to the EPH Method and as such would preclude obtaining "Reasonable Confidence" for any analytical data produced using an alternative EPH extraction procedure.

Table 2.0: Approved EPH Extraction Methods

SW-846 Method	Matrix	Description
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction
3520	Aqueous	Continuous Liquid-Liquid Extraction
3511	Aqueous	Organic Compounds in Water by Microextraction
3535	Aqueous	Solid Phase Extraction (“SPE”)
3540	Soil/ Sediment	Soxhlet Extraction
3541	Soil/ Sediment	Automated Soxhlet Extraction
3545	Soil/ Sediment	Pressurized Fluid Extraction (“PFE”)
3546	Soil/ Sediment	Microwave Extraction
3570	Soil/ Sediment	Microscale Solvent Extraction (“MSE”)
3550	Contaminated Solids[1]	Ultrasonic Extraction
3580	NAPL	Solvent Dilution
[1]Sonication may only be used for the extraction of highly contaminated (free product) non-soil/ sediments (debris). Any other use of ultrasonic extraction is considered a "significant modification" of the EPH Method.		

After solvent exchange with hexane, the extract is concentrated and subjected to a silica gel cleanup and fractionation step to isolate the aromatic and aliphatic components of the sample prior to GC analysis. It should

be noted that the recommended hexane elution volume (20 mL) is critical and may need to be adjusted for each lot of silica gel/cartridges to optimize sample extraction and fractionation efficiencies. See the EPH Method for specifications on the use and evaluation of Fractionation Check Solutions.

Aliphatic and aromatic extracts are introduced into the gas chromatograph separately by directly injecting 1 to 4 µL of each extract using the solvent flush technique. Smaller volumes may be injected if automatic devices are employed. Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with blanks and laboratory QC samples. The sequence ends when the set of sample extracts has been injected or when qualitative and/or quantitative QC criteria are exceeded.

1.3 Method Interferences

Refer to SW-846 Methods 3500, 3600, and 8000 for a detailed discussion of interferences associated with GC methods. Analytical interferences will vary considerably from sample to sample depending on the matrix. While general cleanup techniques are referenced or provided as part of the EPH Method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into four broad categories:

- Contaminated solvents, reagents, or sample processing hardware;
- Contaminated GC carrier gas, parts, column surfaces, or detector surfaces;
- Non-target compounds simultaneously extracted from the sample matrix which cause a detector response; and
- Co-elution of target analytes.

An in-depth discussion of the causes and corrective actions for all these interferences is beyond the scope of this guidance document. A brief discussion of the more prevalent interferences for the EPH Method is presented below.

1.3.1 Chemical Contaminants

The major contaminant source for the EPH Method is attributable to the leaching of plasticizers or other contaminants from silica gel SPE cartridges. Preferably, the silica gel cleanup and fractionation procedure described in the EPH Method should be used to minimize this source of interference.

As described in the EPH Method, peaks identified during the injection of laboratory method blanks, and determined to be attributable to the previously described silica gel SPE cartridge interference, may adversely affect the accurate integration of the C_{11}-C_{22} aromatic hydrocarbon range area. **Subtracting blank values from sample results is not permitted**.

1.3.2 Cross-Contamination/Carryover

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of semi-volatile organic compounds. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever a sample with unusually high EPH Target PAH Analytes and/or range concentrations is encountered, it should be followed by the analysis of a method or solvent blank to check for unacceptable cross-contamination. Concentrations of any EPH target analyte or ranges that exceed the upper limit of calibration should prompt the analyst to check for potential cross-contamination/carryover. Laboratories should be aware that carryover from refractory compounds may compromise a later sample analysis. In addition, samples containing large amounts of water-soluble materials, suspended solids, or high boiling point compounds may also present potential for cross-contamination/carryover. Laboratories should be aware that carryover from high boiling point compounds

may not appear until a later sample analysis. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections.

1.4 Quality Control Requirements for the EPH Method

1.4.1 Reporting Limits/Lower Limits of Quantitation for the EPH Method

These reporting limits ("RL"), or lower limit of quantitation ("LLOQ"), reflect the sampling procedures and prescriptive analytical conditions imposed by the EPH Method. The RL/LLOQs are dependent upon the concentration of the lowest non-zero analytical standard in the initial calibration and/or the percent solids of the sample. RL/LLOQs for the target PAH Analytes and hydrocarbon ranges will be proportionately higher for samples that require dilution, when a reduced sample size is used, or for an increased final extract volume. Table 3.0 lists approximate RL/LLOQs for various matrices utilizing GC/FID. Solid matrices in this table assume 100% solids.

Table 3.0: Typical Report Limits/Lower Limits of Quantitation

Analyte	Matrix	Typical Reporting Limit
Aliphatic & Aromatic Ranges	Water	100 µg/L
	Soil	10 mg/kg
Total Petroleum Hydrocarbons	Water	100 µg/L
	Soil	10 mg/kg
Target PAH Analytes	Water	2 to 5 µg/L
	Soil	0.2 to 1.0 mg/kg

Moisture content of soils and sediments will raise the RL/LLOQ, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL/LLOQs to be raised. It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analytes to meet Remediation Standard Regulation ("RSR") criteria. To meet the limits, it may be necessary to modify the analytical method by using increased sample volume or mass or employing selective ion monitoring. In such cases the modifications must be noted in the laboratory report narrative.

1.4.2 General Quality Control Requirements

This protocol is restricted to use by, or under the supervision of, analysts experienced in the use of GC instrumentation as a quantitative tool and skilled in the interpretation of gas chromatograms for individual Target PAH Analytes and petroleum hydrocarbon ranges in environmental matrices.

Refer to SW-846 Method 8000 for general quality control ("QC") procedures for all chromatographic methods, including the EPH Method. These requirements ensure that each laboratory maintain a formal quality assurance ("QA") program and records to document the quality of all chromatographic data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the GC system operation may be found in the EPH Method and include evaluation of calibrations and chromatographic performance of sample analyses. Instrument QC and method performance requirements for the analytical system may be found in the EPH Method.

The minimum requirements for a formal QA program include Initial Demonstration of Capability ("IDOC"), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples ("LCS") and/ or matrix spikes ("MS") to assess accuracy and LCS duplicates ("LCSD") and matrix spike duplicates ("MSD") to assess precision. The use of site-specific MS/MSD's is highly recommended. Evaluation of sample matrix effects on compound recovery is key to making informed decisions.

Percent recovery data from site-specific samples allow the environmental professional ("EP") to make informed decisions regarding contamination levels at the site. Batch MS/MSD results do not give any indication of site-specific matrix interferences or analytical problems related to the specific site matrices and are in general discouraged. Field, rinsate, or other blanks should not be used for MS/MSD's.

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative analytical method in use. An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform the EPH Method. These data must meet or fall within the performance standards as presented in Section 1.4 and Table 1A of this RCP, in the EPH Method, as presented in SW-846 Method 8000 The IDOC must include the following elements provided in Table 4.0:

Table 4.0: IDOC Requirements

QC Element	Performance Criteria
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Laboratory Method Blanks	Table 1A
Laboratory Control Samples	The EPH Method
Fractionation Check Standard	The EPH Method
Extraction Surrogate Recovery	Table 1A
Fractionation Surrogate Recovery	Table 1A
Potential Aromatic Breakthrough	The EPH Method

Because of the inherent difficulty in quantifying collective hydrocarbon ranges and the number of QC elements associated with the IDOC, it should be expected that one or more of the ranges and/or optional target analytes may not meet the performance standard for one or more QC elements. The laboratory should make every effort to find and correct the problem and repeat the analysis. All non-conforming analytes along with the laboratory acceptance criteria should be noted in the IDOC data. This information should be kept on-file at the laboratory.

Laboratories are required to generate laboratory specific performance criteria for LCS compound recovery limits, matrix spike/matrix spike duplicate compound recovery and relative percent difference ("RPD") limits, and surrogate recovery limits. These limits must be equal to or fall within the limits specified in Table 1A.

1.4.3 Specific QA/QC Requirements and Performance Standards for the EPH Method

Specific QA/QC requirements and performance standards for the EPH Method are presented in Table 1A of this RCP. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide the environmental professional with "Reasonable Confidence" regarding the usability of analytical data to support environmental decisions. The concept of "Reasonable Confidence" is explained on the DEEP website.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will, generally accept "Reasonable Confidence" data. To achieve "Reasonable Confidence" parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate all protocol non-compliances and implement, as necessary, required corrective actions and analytical response actions for all non-conforming analytical performance standards; and

3. Retain reported and unreported analytical data and information for a period of 10 years.

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1.4.4 Additional QA/QC Requirements and Performance Standards Considerations for the EPH Method

The complete list of QA/QC requirements and performance standards described in Table 1A are required only for samples analyzed for both EPH aliphatic and aromatic ranges and Target PAH Analytes. As described in the EPH Method, the analysis of Target PAH Analytes, including the diesel PAH analytes is optional. If these analytes are not reported for a particular sample, then compliance with the applicable QA/QC requirements and performance standards pertaining to these individual analytes is optional. In addition, if fractionation is eliminated and the individual EPH Method aliphatic and aromatic ranges are not quantified then only compliance with the applicable QA/QC requirements and performance standards pertaining to Total Petroleum Hydrocarbon (TPH) analysis is required.

Strict compliance with the applicable QA/QC requirements and performance standards for EPH Method "range-only" or TPH analyses, as well as satisfying the previously described reporting requirements, will still provide an environmental professional with "Reasonable Confidence" regarding the usability of the analytical data to support environmental decisions for these options.

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Table 1A-Specific QA/QC Requirements and Performance Standards for the EPH Method

Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
Initial Demonstration of Capability ("IDOC")	Laboratory Analytical Accuracy& Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must contain all target analytes. (4) Must follow procedure in the EPH method.	No	Refer to the EPH method and Section 1.4.2 of this RCP.	NA	Group accepted MA language.
GC Performance	Inter-Laboratory Consistency & Comparability	(1) PAH resolution as per the EPH method. (2) C_9 resolution from solvent front. (3) Response ratio of C_{28} to C_{20} should be ≥ 0.85. (4) Surrogate and internal standards must be resolved from all aromatic and aliphatic standards. (5) Naphthalene and n-dodecane in the aliphatic fraction must be adequately resolved (see the EPH Method)	No	Perform instrument/injection port maintenance as needed.	Suspend all analyses until performance criteria are achieved. Report exceedances in the laboratory report narrative.	Remove specific Section references to MassDEP EPH Method.
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed.	No	N/A	N/A	Removed specific section references to MassDEP EPH Method.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
		(2) Calculated according to the EPH method. (3) Retention time windows must be updated with every CCV.				
Initial Calibration	Laboratory Analytical Accuracy	(1) Must be analyzed at least once prior to analyzing samples, when initial calibration verification or continuing calibration does not meet the performance standards, and when major instrument maintenance is performed. (2) Minimum of 5 standards (or 6 if non-linear regression is used). (3) Low standard must be ≤ RL/LLOQ. (4) % RSD ≤25, r ≥ 0.990 (linear regression), r^2 ≥ 0.990 (non-linear regression) for all target PAHs and hydrocarbon ranges. (5) If %RSD >25, linear must be used. (6) Must meet GC performance standards described in the EPH method.	No	(1) Recalibrate as required by method. (2) If recalculated concentrations from the lowest calibration standard are outside of 70-130% recovery range, either: (i) The RL/LLOQ must be reported as an estimated value, or (ii) The RL/LLOQ must be raised to the concentration of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration curve.	Sample analysis may not proceed without a valid initial calibration. Report non-conforming compounds (%RSD>25, r<0.99 or r^2<0.99) on laboratory report narrative. If non-linear regression (e.g., quadratic equation) is used for calibration, this must be noted in the laboratory report narrative along with compounds affected.	Group accepted MA language. Column 3, Item 11: Language included to be consistent with the intent of the method.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
		(7) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (8) Calibration must be performed under the same conditions as the samples. (9) If linear or non-linear regression used, verify the RL/LLOQ by recalculating concentrations in lowest calibration standard using the final calibration curve; recoveries must be 70-130%. (10) If regression analysis is used, the curve must not be forced through the origin.				
Initial Calibration Verification ("ICV")	Laboratory Analytical Accuracy	(1) Immediately after each initial calibration. (2) Second source standard. (3) Concentration level near midpoint of curve. (4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method.	No	Locate source of problem; recalibrate if >10% of all analytes are outside of criteria.	If recovery is outside of 70-130% for any target PAH analytes or hydrocarbon range, report non-conforming compounds in laboratory report narrative. Sample analysis may not proceed without a valid ICV.	Column 3, Item 5: Percent recovery range updated to 70-130% based on latest EPH method requirements

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Required Analytical Response Action Column 6	Rationale for Changes (this column will be removed from the final version)
		(5) Percent recoveries must be between 70-130% for all hydrocarbon ranges and target PAH analytes.				
Continuing Calibration Verification ("CCV")	Laboratory Analytical Accuracy	(1) Prior to samples, every 24 hours or every 20 samples, whichever is more frequent, and at the end of the analytical sequence. (2) Concentration near mid-point of curve. (3) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (4) Must meet GC performance standards. (5) Opening CCV: %D must be ≤25 for all target PAH analytes and hydrocarbon ranges. (6) Closing CCV: up to four compounds may exhibit %D or % drift >25 but <40. (7) Verify that all analytes fall within retention time windows.	No	(1) Perform instrument maintenance, reanalyze CCAL and/or recalibrate as required by method. (2) Reanalyze "associated samples" if beginning or ending CCAL exhibited low response. (3) Reanalyze "associated samples" if beginning or ending CCAL exhibited high response and associated target PAHs and hydrocarbon ranges were detected in the "associated samples." NOTE: "Associated samples" refers to all samples analyzed since the last acceptable continuing calibration.	Report non-conforming target PAH analytes or hydrocarbon ranges (%D >25) and associated samples in laboratory report narrative.	Group accepted MA language.
Method Blank ("MB")	Laboratory Method Sensitivity	(1) Extracted with every batch or every 20	Yes	(1) If concentration of contaminant in sample is <10x concentration	(1) If sample re-extraction is not possible, report non-	Group discussed detections below

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Required Analytical Response Action Column 6	Rationale for Changes (this column will be removed from the final version)
	(contamination evaluation)	samples, whichever is more frequent. (2) Matrix-specific (water, soil). (3) Target PAH analytes must be ≤½ RL/LLOQ. (4) EPH hydrocarbon ranges must be ≤½ RL/LLOQ of the most stringent applicable RSR (or APS) standards for solid samples and aqueous samples.		in blank, locate source of contamination; correct problem; re-extract and re-analyze method blank and associated samples (2) No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample.	conformance in laboratory report narrative. (2) If contamination of method blanks is suspected or present, the lab, using a "B" flag or some other convention, should qualify the sample results. Blank contamination should also be documented in the laboratory report narrative. (3) If re-extraction is performed within holding time and yields acceptable method blank results, the lab may report results of the re-extraction only. (4) If re-extraction is performed outside of holding time, the lab must report results of both the initial extraction and re-extraction.	RL/LLOQ, revised language to reflect≤ ≤1/2 the RL/LLOQ to improve the accuracy of the results and to maintain consistency with other RCPs.
Laboratory Control Sample ("LCS")	Laboratory Analytical Accuracy	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Matrix specific (water, soil). (3) Concentration level near midpoint of curve. (4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH method.	Yes	(1) Locate source of problem; re-extract and re-analyze LCS and associated samples if target PAH analytes or hydrocarbon ranges are outside of criteria. (2) If target PAH analytes or hydrocarbon ranges are above the acceptance criteria (>140%), re-extraction	(1) If sample re-extraction is not possible, report non-conformance in laboratory report narrative. (2) If recovery is outside of 40-140% for any target PAH analyte or hydrocarbon range, report non-conforming analytes/ranges in laboratory report narrative. (3) If re-extraction or re-fractionation is performed	Group accepted MA language. Column 3, Item 5: Included range exception for n-nonane to be consistent with the intent of the method. Colum 3: Language

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Required Analytical Response Action Column 6	Rationale for Changes (this column will be removed from the final version)
		(5) Percent recoveries must be between 40-140% for target PAH analytes and hydrocarbon ranges, except for n-nonane which must be between 30-140%. (6) Individual concentrations of both naphthalene and 2-methylnaphthealene must be <5% in aliphatic fraction. (See calculation in the EPH Method). (7) Prepared using standard source different than used for initial calibration. (8) Must be prepared in a water-miscible solvent (e.g., acetone, methanol).		is not required if affected analytes/hydrocarbon ranges were not detected in associated samples. (3) If LCS is re-extracted and still outside of criteria, recalibration is required. (4) Re-fractionate archived batch extracts if either the concentration of naphthalene and/or 2-methylnaphthalene in aliphatic fraction is >5% of either of their respective total concentrations.	within holding time and yields acceptable LCS results, the lab may report results of the re-extraction or re-fractionation only. (4) If re-extraction or re-fractionation is performed outside of holding time, the lab must report results of both the initial extraction and re-extraction or re-fractionation.	regarding laboratory established limits was moved to RCP Section detailing IDOC requirements.
LCS Duplicate ("LCSD")	Laboratory Analytical Accuracy & Precision	(1) Extracted with every batch or every 30 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level near midpoint of curve. (4) Must contain all aliphatic and aromatic	Yes	(1) Locate source of problem; re-extract and re-analyze LCS and associated samples if >10% of all analytes are outside of recovery acceptance criteria. (2) If ≤10% of compounds are outside of the recovery acceptance criteria, re-extraction is not	(1) If sample re-extraction is not possible, report non-conformance in laboratory report narrative. (2) If recovery is outside of 40-140% or RPD >25 for any analyte, report non-conforming compounds in laboratory report narrative. (3) If re-extraction or re-fractionation is performed within holding time and	Group accepted MA language. Colum 3, Item 7: Removed references to specific EPH methods.

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Required Analytical Response Action Column 6	Rationale for Changes (this column will be removed from the final version)
		hydrocarbon standards listed in Tables 1 and 2 of EPH method. (5) Matrix-specific (e.g., water, soil). (6) Percent recoveries must be between 40-140% for target analytes and hydrocarbon ranges, except for nonane which must be between 30-140%. (7) The individual concentrations of both naphthalene and 2-methylnaphthalene must be <5% in aliphatic fraction. (See calculation in the EPH Method (8) RPDs must be ≤25 for waters and solids. (9) Must be prepared in a water-miscible solvent (e.g., acetone, methanol).		required as long as recoveries are >10%. (3) If >10% of compounds are above the recovery acceptance criteria (>140%), re-extraction is not required if affected compounds were not detected in associated samples. (4) Re-fractionate archived batch extracts if either the concentration of naphthalene and/or 2-methylnaphthalene in aliphatic fraction is >5% of either of their respective total concentrations.	yields acceptable LCS results, the lab may report results of the re-extraction or re-fractionation only. (4) If re-extraction or re-fractionation is performed outside of holding time, the lab must report results of both the initial extraction and re-extraction or re-fractionation.	
Matrix Spike / Matrix Spike Duplicate ("MS/MSD") (Site specific)	Method Accuracy & Precision in Sample Matrix	(1) Every 20 samples (at discretion of lab or at request of data user). (2) Prepared using standard source different from initial calibration. (3) Concentration level near the midpoint of curve.	Yes ONLY when requested by data user	Check LCS; if recoveries are acceptable in LCS, narrate non-conformance.	Note non-conformances in laboratory report narrative.	Group accepted MA language. Column 3, Item 6: Included range exception for n-nonane to be consistent with the intent of the method.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
		(4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH method. (5) Matrix-specific (e.g., water, soil). (6) Percent recoveries must be between 40-140% for target PAH analytes and hydrocarbon ranges, except for nonane which must be between 30-140%. (7) RPDs ≤50% for waters and solids. (8) Must be prepared in water-miscible solvent (e.g., acetone, methanol). (9) Field blanks, trip blanks, etc. cannot be used for MS/MSDs.				
Matrix Duplicates ("MD")	Method Precision in sample matrix	(1) Every 20 samples (at discretion of laboratory or at request of data user). (2) Matrix-specific (water, soils). (3) RPDs should be ≤50% for waters and solids for results >5x the RL/LLOQ.	Yes ONLY when requested by data user	(1) If RPD >50% and both results are >5x the RL/LLOQ, repeat analysis. (2) If a target PAH analyte or hydrocarbon range is detected in one analysis at >5x the RL/LLOQ and not detected in the	Note non-conformances (RPDs>50%) in laboratory report narrative.	Group accepted MA language.

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Required Analytical Response Action Column 6	Rationale for Changes (this column will be removed from the final version)
				duplicate analysis, repeat analysis. (3) Re-check RPD calculations.		
Surrogates	Method Accuracy in Sample Matrix	(1) Minimum of 2 extraction surrogates and 1 fractionation surrogate: (i) Recommended extraction surrogates: COD and OTP. (ii) Recommended fractionation surrogates: 2-bromonaphthalene and 2-fluorobiphenyl (optional). (2) Percent recoveries must be between 40-140% for all surrogates.	Yes	If one or more surrogates are outside of limits or if any one surrogate recovers at <10%: (1) Re-extract the sample or re-fractionate the appropriate extract if surrogate recoveries are low. (2) Re-extract the sample or re-fractionate the appropriate extract if surrogate recoveries are high and associated aliphatic or aromatic analytes were detected in the sample. (3) Re-extraction or re-fractionation is not required if one of the following exceptions applies: (i) If surrogate recoveries are high and associated target analytes are not detected in sample.	(1) Report recoveries outside of 40-140% laboratory report narrative. Note non-conformances in laboratory report narrative. (2) If re-extraction yields similar surrogate non-conformances, the lab must report results of both the initial extraction and re-extraction. (3) If re-extraction or re-fractionation is performed within holding time and yields acceptable surrogate recoveries, the lab may report results of the re-extraction or re-fractionation only. (4) If re-extraction or re-fractionation is performed outside of the holding time and yields acceptable surrogate recoveries, the lab must report results of both the initial extraction/fractionation and re-extraction/re-fractionation. (5) If sample is not re-extracted or re-fractionated due to obvious interference,	Group accepted MA language.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
				(ii) If obvious interference present (e.g., UCM). NOTE: If obvious interference is present and surrogate recovery would cause rejection of data (<10%), re-analyze sample on dilution. (iii) If a surrogate is diluted to a concentration below that of the lowest calibration standard, re-extraction and/or re-analysis is not required. NOTE: OTP non-conformances affect the targe PAH analytes and C_{11}-C_{22} aromatic hydrocarbons; COD non-conformances affect the C_9-C_{18} and C_{19}-C_{36} aliphatic hydrocarbons.	the lab must provide the chromatogram in the data report.	
Internal Standards (for GC/MS used for quantification of targe PAH analytes and aliphatic/aromatic	Laboratory Analytical Accuracy & Method Accuracy in Sample Matrix	(1) Minimum of 1. Recommended internal standard is 5-alpha androstane. Alternatively, COD may also be as an internal	No	If internal standard is outside of limits, reanalyze sample unless obvious interference present (UCM).	(1) Report non-conformances in laboratory report narrative. Include actual recovery of internal standard and provide summary of analytes	Group accepted MA language.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
hydrocarbon ranges after fractionation)		standard for GC/MS analysis. (2) Area counts in samples must be between 50-200% of the area counts in the associated continuing calibration standard. (3) Retention Times of internal standards must be within ± 30 seconds of retention times in associated continuing calibration standard.		NOTE: If obvious interference is present and internal standard area would cause rejection of data (<20%), reanalyze sample on dilution.	quantitated using the internal standard. (2) If reanalysis yields similar internal standard non-conformances, the lab must report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recoveries, the lab may report results of the reanalysis only. (4) If reanalysis is performed outside of the holding time and yields acceptable internal standard recoveries, the lab must report results of both analyses. (5) If sample is not reanalyzed due to obvious interference, the lab must provide the chromatogram in the data report.	
Fractionation Check	Laboratory Method Accuracy	(1) Performed for each new lot of silica gel cartridges. (2) Must contain all EPH aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (3) Percent recoveries must be between 40-140% for EPH	Yes	Re-fractionate using different volumes of hexane until recoveries are acceptable.	Report recoveries outside of 40-140% in laboratory report narrative.	Group accepted MA language with the exception of Colum 4; the group decided that the fractionation check should be a required deliverable.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
		hydrocarbon ranges and target PAH analytes except for n-nonane, which must be between 30-140%.				
Quantitation	NA	(1) The lab must use the average calibration factor, response factor, linear or non-linear regression curve generated from the associated initial calibration for quantitation of each target PAH analyte and hydrocarbon range. (2) Do not report concentrations below the RL/LLOQ.	NA	NA	NA	Group accepted CAM language with the exception of the significant figures because CT does not advise reporting values <RL.
Identification	NA	Refer to the EPH Method.	NA	NA	NA	Group accepted MA language.
Sample Specific Breakthrough (when GC/MS used for quantification of target PAH analytes and aliphatic/aromatic hydrocarbon ranges after fractionation)	Laboratory Method Accuracy in Sample Matrix	(1) The laboratory must measure the concentrations of naphthalene and 2-methylnaphthalene in the aliphatic fraction of each sample. (2) The concentration of naphthalene or 2-methylnaphthalene in the aliphatic fraction must be ≤5% of the total concentration of naphthalene or 2.	Yes	Re-fractionate the archived sample extract if >5%.	Report naphthalene and 2-methylnaphthalene results which exceed 5% of the total in the laboratory report narrative.	Group accepted MA language.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Required Analytical Response Action** Column 6	**Rationale for Changes (this column will be removed from the final version)**
General Reporting Issues	NA	(1) The lab must only report values ≥ than the sample-specific RL/LLOQ. (2) Dilutions- if diluted and undiluted analyses are performed, the lab should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (method blank, surrogates) for each analysis must be reported. (3) All information required in this RCP method must be provided for each sample. (4) Results for soils/sediments must be reported on a dry-weight basis. (5) Concentrations below the reporting limit should be report as "ND" with the sample specific RL/LLOQ also reported.	NA	NA	(1) The performance of dilutions must be documented in the laboratory report narrative or on the report form. Unless due to elevated concentrations of target PAH analytes or hydrocarbon ranges, reasons for dilutions must be explained in the laboratory report narrative. (2) Complete analytical documentation for diluted and undiluted analyses must documented in laboratory report narrative and be maintained in laboratory records. (3) If samples are not properly preserved (pH >2 for aqueous samples) or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory report narrative. (4) If samples are extracted and/or analyzed outside of the holding time, note the non-conformances in the laboratory report narrative.	Group accepted MA language. Colum 3, Item 2: MA language adopted to remain consistent with the intent of the Method. Column 6: CT does not conduct audits, therefore group did not adopt CAM language regarding record retention for audit purposes.
If the RL/LLOQ is estimated due to unacceptable recovery of the lowest standard, the RL/LLOQ has not been achieved; Question 5b of the "Reasonable Confidence Protocol Laboratory Analysis QA/QC Certification Form" must be answered "NO" and this must be addressed in the laboratory report narrative.						

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1.5 Analyte List for the EPH Method

As described in Section 1.1, the EPH Method is designed to complement and support the toxicological approach developed by DEEP to evaluate human health hazards that may result from exposure to petroleum hydrocarbons. It is intended to produce data in a format suitable for evaluation by that approach.

The DEEP analyte list for the EPH Method is presented in Table 1B. The list is comprised of seventeen (17) PAH Analytes, four (4) of which are required for the evaluation of diesel fuel releases, and three (3) collectively quantified extractable hydrocarbon ranges, as identified in the EPH Method, that are readily analyzable using (1) the extraction methods described in Table 2.0, (2) the cleanup and fractionation procedure described in of the EPH Method, and (3) conventional GC/FID separation and analysis. All the Target PAH Analytes and hydrocarbon ranges that comprise the RCP Analyte List for the EPH Method have hydrocarbon range (e.g., C11-C22 aromatic hydrocarbons) or compound-specific water or soil criteria as described in the RSRs. Use of the EPH Method to identify and quantify the listed Target PAH Analytes is optional at the discretion of the data user.

Table 1B: Analyte List for the EPH Method

Range/ Optional Target Analyte	CAS No.
EPH Ranges	
C9 - C18 Aliphatic Hydrocarbons	N/A
C19 - C36 Aliphatic Hydrocarbons	N/A
C11 - C22 Aromatic Hydrocarbons	N/A
Diesel PAH Analytes	
Naphthalene	91-20-3
2-Methylnaphthalene	91-57-6
Phenanthrene	85-01-8
Acenaphthene	83-32-9
Other Target PAH Analytes	
Fluorene	86-73-7
Acenaphthylene	208-96-8
Anthracene	120-12-7
Fluoranthene	206-44-0
Pyrene	129-00-0
Benzo(a)anthracene	56-55-3
Chrysene	218-01-9
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(a)pyrene	50-32-8
Indeno(1,2,3-cd)pyrene	193-39-5
Dibenz(a,h)anthracene	53-70-3
Benzo(g,h,i)perylene	191-24-2

1.5.1 Additional Reporting Requirements for the MassDEP EPH Method

While it is not necessary to request and report all the Target PAH Analytes listed in Table 1B, it is required to quantify the EPH aliphatic and aromatic hydrocarbon ranges, described in the same table, to obtain "Reasonable Confidence" status. Such limitations must be documented for site characterization and data representativeness considerations. DEEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous

materials. It is also permissible to quantify EPH Target PAH Analytes, and aliphatic and/or aromatic range concentrations by GC/MS using a "modified" SW-846 Method 8270 as described in the EPH Method.

In cases where a shortened list of analytes is selected, the laboratory must still meet the method specific quality control requirements and performance standards associated with the requested analytes list to obtain Reasonable Confidence.

1.6 Routine Reporting Deliverables for the EPH Method

The following table (Table 5.0) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report these items in special circumstances.

Table 5.0: Report Deliverables

Parameter	Deliverable	Comments
GC Performance	NO	
Retention Time Windows	NO	
Initial Calibration	NO	Note non-conformances in laboratory report narrative
Initial Calibration Verification	YES	Note non-conformances in laboratory report narrative
Continuing Calibration Verification	NO	Note non-conformances in laboratory report narrative
Method Blanks	YES	Note non-conformances in laboratory report narrative. Flag all positive results above RL/LLOQ with “B” flag.
Laboratory Control Sample/Lab Control Sample Duplicate	YES	Note non-conformances in laboratory report narrative
Matrix Spike/ Matrix Spike Duplicate	YES (if requested by data user)	Note non-conformances in laboratory report narrative
Matrix Duplicate	YES (if requested by data user)	Note non-conformances in laboratory report narrative
Extraction Surrogates	YES	Note non-conformances in laboratory report narrative
Fractionation Surrogates	YES	Note non-conformances in laboratory report narrative
Fractionation Check Standard	YES	Note non-conformances in laboratory report narrative
Aromatic Breakthrough Evaluation	YES	Note non-conformances in laboratory report narrative
System Solvent Blank (for baseline correction only)	YES (See the EPH Method)	Note non-conformances in laboratory report narrative
GC/MS QC Parameters	YES (GC/MS only)	Note non-conformances in laboratory report narrative

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Parameter	Deliverable	Comments
General Reporting Issues	YES	Note non-conformances in laboratory report narrative
QA/QC Certification Form	YES	Signed by laboratory director or their designee
Chain-of-Custody Form	YES	Signed by sample collector, courier, and laboratory.

1.6.1 Reporting and Flagging of Results

The following rules apply to reporting results:

- Non-Detects: Report all non-detects and results below the reporting limit as "ND" (Not Detected at the Specified RL/LLOQ). The RL/LLOQ for each compound in each sample must be listed on the report, based upon the lowest calibration standard, the exact sample mass, any dilution factors, percent moisture, etc.
- Compounds detected above the RL/LLOQ in blanks and in samples shall be flagged with a "B" suffix (e.g., 25B).
- Report results for any library search compounds as estimated using a "J" suffix (e.g., 25J).
- All soil/sediment results shall be reported on a dry weight basis.

1.7 Sample Containers, Preservation, and Holding Times

Table 6.0 identifies the type of containers, preservation requirements, and holding times dependent upon analyte and matrix.

Table 6.0: Sample Containers, Preservations, and Holding Times

Matrix	Container Type[1]	Preservation[2]	Holding Time
Aqueous	1-Liter amber glass with Teflon-lined screw cap	Add 1:1 HCl to pH <2 Cool to 4 ± 2º C	Samples must be extracted within 14-days of collection. Extracts must be analyzed within 40-days of extraction.
Soil/ Sediments	4-oz. (120 mL) wide mouth amber jar with Teflon-lined screw cap	Cool to 4 ± 2º C	Samples must be extracted within 14-days of collection. Extracts must be analyzed within 40-days of extraction.
	4-oz. (120 mL) wide mouth amber jar with Teflon-lined screw cap. Jar should be filled only 2/3 full to avoid breakage if expansion occurs during freezing.	Freeze at -12 ± 3º C[3]	Samples must be extracted within 14 days of thawing and extracts must be analyzed within 40-days of extraction.
Waste	1-500 mL wide mouth amber jar with Teflon-lined screw cap.	Cool to 4 ± 2º C	Samples must be extracted within 14-days of collection. Extracts must be analyzed within 40-days of extraction.

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[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6°C are acceptable.

[3]Soil/sediment samples processed in the laboratory must be preserved at 4 ± 2º C and frozen within 48-hours of collection. May be held for up to one (1) year if frozen within 24 hours of collection at <-10°C. Once the thawing process begins, samples must be kept at 0-6°C until extraction. Temperature must never be allowed to go below –20°C to avoid damage to seals, etc.

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Appendix 1: EPH Data Usability Assessment for MassDEP EPH Method

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A-1 Data Usability Assessment for the EPH Method

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for the EPH Method, which may be used to directly assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

A-1.1 Specific Guidance Regarding the Interpretation and Use of EPH Data

The EPH Method produces both analyte-specific (Target PAH Analytes) and method defined (hydrocarbon fractions) data. An analyte-specific approach produces data by comparing the response of a known analyte with an unknown concentration to the response of a standard for the same analyte with a known concentration under the same analytical conditions. A method-defined approach produces data by prescriptively defining both analytical conditions and assumptions used to calibrate and interpret the data produced. Such an approach is particularly useful in determining average characteristics for a limited set of analytes with similar physical, chemical and toxicological properties (i.e., the collective concentration of a limited range of hydrocarbons). However, a clear understanding of the analytical limitations of the method and assumptions used to interpret data are required to maximize the potential of using this approach.

Both EPH Target PAH Analytes and ranges are subject to potential "false positive" bias associated with non-specific gas chromatographic analysis. That is (1) other compounds co-eluting at the specified retention time may be incorrectly identified and/or quantified (false positive) as a Diesel or Target PAH Analyte; (2) compounds not meeting the regulatory definition of the aromatic and/or aliphatic fractions as defined by this method in the EPH Method, respectively, that elute within the method-defined retention time window would be included in the Peak Area Count (PAC) and result in an overestimation of a fraction's concentration; (3) as described in the EPH Method, the lighter aromatic compounds may be stripped or may break through the silica gel cartridge/column because of mass overloading or excessive eluting solvent volume, resulting in an underestimation of the C_{11} through C_{22} aromatic fraction's concentration; or, (4) also as described in the EPH Method, insufficient eluting solvent volume may allow aliphatic hydrocarbons to be retained on the silica gel cartridge/column resulting in low recoveries of these fractions.

Confirmatory analysis by a GC/MS procedure or other suitable method is recommended in cases where a Target or Diesel PAH Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a hydrocarbon compound not meeting the regulatory definition of a specific hydrocarbon fraction is suspected. ***Dual-column confirmation is suitable for confirmation of optional Target PAH Analytes only.***

The following definitions are provided to assist in the interpretation and evaluation of EPH data:

Aliphatic Hydrocarbon: Any organic compound comprised solely of carbon and hydrogen characterized by a straight, branched or cyclic chain of carbon atoms. This class of organic compounds includes alkanes, alkenes, alkynes, cycloalkanes or cycloalkenes.

Aromatic Hydrocarbon: Any cyclic and conjugated organic compound comprised solely of carbon and hydrogen. Aromatic compounds of environmental significance are benzoids that contain benzene or fused benzene rings.

EPH: Any hydrocarbon that elutes within the C_9 through C_{18} and C_{19} through C_{36} aliphatic, or the C_{11} through C_{22} aromatic ranges defined by the method. The definition of Extractable Petroleum Hydrocarbon specifically **excludes** all substituted aliphatic or aromatic hydrocarbon derivatives (non-hydrocarbons as defined by the EPH Method), the individual EPH Method Target and Diesel PAH Analytes, surrogates, and/or internal standards that co-elute within these method-specific ranges. The EPH Method is suitable for the separation and

quantification of the aliphatic and non-target aromatic components of kerosene, fuel oil #s 2, 4 and 6, diesel fuel, jet fuel (JP-4, 5 and 8) and certain hydrocarbon-based, low to medium viscosity lubricating oils contained within the aforementioned method-defined ranges (C_9 through C_{36}). These aliphatic hydrocarbon ranges correspond to a boiling point range between approximately 150°C and 265°C. Consequently, the EPH Method, in and of itself, is not suitable for the evaluation of lower boiling petroleum products (gasoline, mineral spirits, or certain petroleum naphthas) or higher boiling petroleum products (asphalts, tars, etc) outside the dynamic range of this method.

Total Petroleum Hydrocarbons ("TPH"): The collective concentration associated with the PAC for all peaks corresponding to any fractionated or unfractionated aliphatic and/or aromatic compounds eluting between 0.1 minutes before the retention time for n-C_9 to 0.1 minutes after the Rt for n-C_{36}, **excluding** the PAC for all substituted aliphatic or aromatic hydrocarbon derivatives, the individual EPH Method Target and Diesel PAH Analytes, surrogates, and/or internal standards that co-elute within this chromatographic range. The CTDEEP recommends that the analysis of the unfractionated EPH extract be used as a conservative estimate of TPH when this parameter is used to support human health risk characterization or other assessments and evaluation decisions.

A-1.1.1 Interfering Peaks in Specified Aliphatic Hydrocarbon Ranges

Hydrocarbons (and non-hydrocarbons), even with elution times within the defined chromatographic windows for the aliphatic hydrocarbon ranges specified by the EPH Method, need not be included in the PAC for these ranges unless they meet the definitions of aliphatic hydrocarbon and extractable petroleum hydrocarbon, as defined above. If the concentration of a hydrocarbon range is based on one (or just a few) peaks within the range and an indicative petroleum hydrocarbon peak pattern is not apparent, the laboratory should provide this information and alert the data user of the potential for a false positive result in the laboratory report narrative. Sites with co-mingled non-petroleum hydrocarbons such as vegetable oils, synthetic oils and lubricants, and some naturally occurring humic materials are particularly susceptible to this type of interference.

A-1.1.2 Interfering Peaks in Specified Aromatic Hydrocarbon Range

The EPH Method should be used with caution at sites with uncertain history and disposal practices, particularly at sites where other hazardous materials were used, stored and/or managed. Such contaminants, if encountered, may co-elute within the method-defined aliphatic and or aromatic ranges resulting in an overestimation of the concentration (i.e., positive interference).

A-1.1.3 Evaluation of Individual Hydrocarbons Not Associated with an Extractable Petroleum Hydrocarbon

In general, it may be prudent to confirm all FID data using SW-846 Method 8270 (GC/MS) if critical environmental decision-making (notification, compliance with cleanup standards, risk assessment, etc.) is based solely on the EPH Method (or any other non-specific GC analysis). If a positive interference is suspected from hydrocarbons and/or non-hydrocarbons not associated with EPH in either aliphatic or the aromatic fraction or with a Target or Diesel PAH Analyte, and such interference would adversely affect decision-making, if confirmed, then SW-846 Method 8270, Semi-Volatile Organics by GC/MS, should be employed to accurately identify and quantify the components that comprise a fraction or to resolve any uncertainty regarding the identification of a specific Target or Diesel PAH Analyte.

It is recommended that the chromatographic conditions specified under SW-846 Method 8270 be modified for consistency with the conditions specified by the EPH Method to better allow for a direct comparison of the suspect FID peaks with the GC/MS system. This is particularly useful when comparing "suspect" aliphatic

hydrocarbons. The electron impact mass spectra for aliphatic hydrocarbon homologues are not particularly unique and chromatographic relative retention time data may also be required to confirm suspect EPH data.

A-1.1.4 Ineffective Separation of Aromatic and Aliphatic Fractions During Silica Gel Cleanup and Fractionation Step

The amount of hexane used to elute the aliphatic component of the EPH hydrocarbon mixture is critical. An excessive volume of hexane may cause the lighter aromatics to breakthrough and be captured in the aliphatic fraction; while an insufficient volume of hexane may allow some of the heavier aliphatic hydrocarbons to be retained on the silica gel cartridge/column resulting in a lower recovery for these aliphatic fractions. Depending on the analytical conditions, this could result in an underestimation of the C_{11} through C_{22} aromatic fraction's concentration for the excessive hexane condition or an overestimation of the aromatic fraction for the deficient hexane condition. It should be noted that acceptable recovery of the Fractionation Surrogate Standards, described in the EPH Method, may not always provide absolute confirmation that effective separation of the aliphatic fraction from the aromatic fraction of the sample extract has been accomplished.

If ineffective fraction separation is suspected, even with acceptable recovery of the Fractionation Surrogate Standards, SW-846 Method 8270, Semi-Volatile Organics by GC/MS, may be employed to accurately identify and quantify the components that comprise a suspect fraction to resolve the uncertainty. Alternatively, if aromatic breakthrough is suspected, the aliphatic fraction may be analyzed to determine if naphthalene or any of the other more "mobile" aromatics are present. See EPH Method for more detail.

If ineffective fraction separation is confirmed, the elution volume for optimal fractionation efficiency for the specific silica gel lot should be re-established as described in the EPH Method. ***For particularly difficult separations, it may be required to resort to multiple cartridge or column cleanup/fractionation.***

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Appendix 2: Substitution of GC/MS for the Identification and Quantification of Ranges and Target Analytes

A-2.1 Substitution of GC/MS for the Identification and Quantification of Ranges and Target Analytes

Consistent with the Data Reporting Section of the EPH Method, use of a GC/MS detector operated in the Total Ion Current mode to quantify the EPH Method's aliphatic and aromatic hydrocarbon ranges is not considered a "significant modification" provided that:

- The sample extract has been **fractionated**;
- The GC/MS system was also used to identify and quantify the Target PAH Analytes in the sample's aromatic fraction; and
- The QC requirements and performance standards specified in the EPH Method are satisfied.

The EPH Method allows for "significant modifications", such as the use of a GC/MS detector to identify and quantify the EPH aliphatic and aromatic hydrocarbon ranges of an **un-fractionated** sample extract, provided that adequate documentation exists, or has been developed to demonstrate an equivalent or superior level of performance. Be advised, however, that any adaptation to the EPH Method that constitutes a "significant modification" pursuant to The Data Reporting Section will preclude obtaining "Reasonable Confidence" status for any analytical data produced using such modification and must be disclosed and documented on an attachment to the EPH Method analytical report form, as described in the EPH Method and Appendix 1 of this Method.

Any major modification to the EPH Method is deemed to satisfy the requirement "to demonstrate an equivalent or superior level of performance" for the determination of the collective concentrations of specified EPH aliphatic and aromatic ranges in water and soil/sediment matrices when:

1. The analytical data produced by the candidate method modification is in a format that is suitable for the evaluation using the toxicological approach developed by DEEP to evaluate human health hazards that may result from exposure to petroleum hydrocarbons;

2. The analytical data produced by the candidate method modification for both the EPH aliphatic and aromatic ranges and Target PAH Analytes must have the requisite accuracy and precision to be compared to reporting and cleanup standards;

3. The reported concentration for the C_9 - C_{18} Aliphatic Hydrocarbon range includes the preponderance of the individual C_9 through C_{18} aliphatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment;

4. The reported concentration for the C_{19} .C_{36} Aliphatic Hydrocarbon range includes the preponderance of the individual C_{19} through C_{36} aliphatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment; and,

5. The reported concentration for the C_{11} - C_{22} Aromatic Hydrocarbon range includes the preponderance of individual C_{11} through C_{22} aromatic hydrocarbon compounds contained in the subject petroleum product in the matrix of interest associated with a release to the environment.

A-2.2 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the EPH target PAH analytes or hydrocarbon ranges exceed the concentration of their respective highest calibration standard, or any non-target peak exceeds the dynamic range of the detector (i.e., off scale.), the RL/LLOQ each EPH target PAH analyte or hydrocarbon range must be adjusted (increased) in direct proportion to the Dilution Factor (“DF”). Where the revised RL/LLOQ for the diluted sample extract is defined as “RLd”:

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RLd = DF x Lowest Calibration Standard for Target PAH Analyte (or hydrocarbon range)

Sample extracts with elevated RL/LLOQs as a result of a dilution may not be able to satisfy CTDEEP regulatory criteria in some cases if the RLd is greater than the applicable standard or criterion to which the concentration is being compared. Such increases in RL/LLOQs are the unavoidable but acceptable consequence of sample extract dilution that enables quantification of target analytes or ranges, which exceed the calibration range. All dilutions must be fully documented in the laboratory report narrative.

Analytical Note: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the highest concentration target analyte in the sample extract must be at least 60 to 80% of its highest calibration standard. This will avoid unnecessarily high reporting limits for other target analytes, which did not require dilution.

If a sample analysis results in a saturated detector response for any target or non-target compound, the analysis must be followed by a System Solvent Blank analysis. If the solvent blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a solvent blank demonstrates the lack of system interferences.