SELECTION OF ANALYTICAL METHODS TO CHARACTERIZE PETROLEUM RELEASES GUIDANCE DOCUMENT

DRAFT FOR PUBLIC COMMENT

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Commissioner Robert Klee

CONNECTICUT DEPARTMENT OF ENERGY & ENVIRONMENTAL PROTECTION
79 Elm Street, Hartford, CT 06106-5127
www.ct.gov/deep
(860) 424-3705

PREAMBLE

The Connecticut Department of Energy and Environmental Protection (DEEP) developed this guidance document to provide information to assist the environmental professional in the selection of appropriate analytical methods for the characterization of petroleum releases. This guidance is based on the recommendations of the DEEP Remediation Division's Laboratory Quality Assurance/Quality Control Work Group (Work Group). The Work Group is comprised of licensed environmental professionals (LEPs), data validators, representatives from private laboratories, the Connecticut Department of Public Health (DPH), the U.S. Environmental Protection Agency (EPA), and the DEEP. The DEEP gratefully acknowledges the contributions and assistance of those individuals who volunteered their time and effort to help develop and prepare this document.

Spills and releases of petroleum products are a leading source of environmental contamination. Petroleum products are a complex and highly variable mixture of individual hydrocarbons. The Remediation Standard Regulations (RSRs), sections 22a-133k-1 through 22a-133k-3 of the Regulations of Connecticut State Agencies (RSCA), as originally promulgated, contained criteria for Total Petroleum Hydrocarbons based on a method that utilized Freon-113 (Method 418.1). In an effort to help bring about the end of Freon use in Connecticut and to be consistent with Federal Law, the DEEP will not accept analytical data derived by EPA Method 418.1 for samples collected on or after June 30, 2009.

Releases of petroleum products may be characterized through the use of various methods, including, but not limited to:

- Extractable Total Petroleum Hydrocarbons (ETPH)
- Extractable Petroleum Hydrocarbons (EPH)
- Volatile Petroleum Hydrocarbons (VPH)
- Air-Phase Petroleum Hydrocarbons (APH)
- Method 8260
- Method 8270

At the time of the publication of this document, the RSRs do not include criteria associated with data generated by the EPH, VPH, and APH methods. Until such time as such criteria are promulgated in the RSRs, requests to use these methods and associated analytical results may be submitted for the Commissioner's review and approval, on a site-specific basis, as Additional Polluting Substances (or

Alternative Criteria). Reasonable Confidence Protocols are provided for the Quality Assurance and Quality Control (QA/QC) for the above methods excluding APH.

This overview is designed to answer general questions and provide basic information. The information contained in this guidance document is intended to provide information to assist the environmental professional in selecting appropriate analytical methods for the characterization of petroleum releases and does not constitute the Department's interpretation of the applicable laws. The environmental professional should refer to the appropriate statutes and regulations and comply with applicable laws. Nothing in this document should be viewed as limiting or obviating the need for the exercise of good professional judgment.

This document excludes radiological issues including, but not limited to, those described in Title 22a Chapters 446 and 446A that are overseen by the DEEP Monitoring and Radiation Division of the Bureau of Air Management. This document does not apply to Polychlorinated Biphenyls pursuant to the Title 40 Code of Federal Regulations (CFR) Part 761.

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LIST OF ACRONYMS

APH	Air-Phase Petroleum Hydrocarbons
APS	Additional Polluting Substance
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CFR	Code of Federal Regulations
CSM	Conceptual Site Model
DEEP	Connecticut Department of Energy and Environmental Protection
DPH	Connecticut Department of Public Health
DQO	Data Quality Objective
EDB	Ethylene dibromide
EPA	United States Environmental Protection Agency
EPH	Extractable Petroleum Hydrocarbons
ETPH	Extractable Total Petroleum Hydrocarbons
GWPC	Ground Water Protection Criterion
LEP	Licensed Environmental Professional
MDL	Method Detection Limit
MTBE	Methyl-tert-butyl ether
µg/l	Micrograms per Liter
PAHs	Polycyclic Aromatic Hydrocarbons, also known as Polynuclear Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
QA/QC	Quality Assurance/Quality Control

RCP(s) Reasonable Confidence Protocol(s)

RCSA Regulations of Connecticut State Agencies

RL Reporting Limit

RSRs Remediation Standard Regulations of the Regulations of Connecticut State Agencies, Sections 22a-133k-1 through 22a-133-3, inclusive

SCGD Site Characterization Guidance Document, effective September 2007, Connecticut Department of Environmental Protection or most recent version

SVOCs Semi-volatile Organic Compounds

TAME Tert-Amyl methyl ether

TBA Tertiary butyl alcohol

TPH Total Petroleum Hydrocarbons

VOCs Volatile Organic Compounds

VPH Volatile Petroleum Hydrocarbons

Work Group Connecticut Department of Energy and Environmental Protection Remediation Division Laboratory Quality Assurance Quality Control Work Group

DEFINITION OF TERMS

Term	Definition
Additional Polluting Substance	Any substance for which a Direct Exposure, Pollutant Mobility, or Groundwater Protection criterion is not specified in sections 22a-133k-1 through 22a-133k-3, inclusive, of the Regulations of Connecticut State Agencies.
Additive	Any compound added to the normal formulation of the specified product. For example, tetraethyl lead, ethylene dibromide (EDB), and later Methyl-tert-butyl ether (MTBE) were additives to gasoline that are no longer used. Current additives, which are added to gasoline to boost the octane level, include tertiary butyl alcohol (TBA), ethanol, tert-Amyl methyl ether (TAME), and others.
Air-Phase Petroleum Hydrocarbons	Air-Phase Petroleum Hydrocarbons are defined as collective ranges of hydrocarbon compounds eluting from isopentane to n-dodecane, excluding Target APH Analytes. APH is comprised of C5-C8 aliphatic hydrocarbons, C9-C12 aliphatic hydrocarbons, and C9-C10 aromatic hydrocarbons.
Aliphatic Hydrocarbon	A straight-chain hydrocarbon compound consisting of hydrogen and carbon only.
Analytical Method	Laboratory method or technique used to determine the concentration of a compound, chemical element, or group of compounds.
Aromatic Hydrocarbon	A compound which contains one or more benzene rings.
Carbon Range	The compounds which elute in a given retention-time window as defined by method-specified markers. For example, the C9 to C12 aliphatic carbon range refers to compounds that elute between nonane (C9) and dodecane (C12).
Environmental Professional	An individual who has specific education, training, and experience necessary to exercise sound professional judgment to develop conclusions regarding conditions indicative of releases or potential releases at a site as defined in the State of

	Connecticut, Department of Environmental Protection, Site Characterization Guidance Document, effective September 2007, page vi.
Extractable Petroleum Hydrocarbons	Extractable Petroleum Hydrocarbons (EPH) are defined as collective fractions of hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, excluding Target polycyclic aromatic hydrocarbons (PAH) Analytes. EPH is comprised of C9 through C18 Aliphatic Hydrocarbons, C19 through C36 Aliphatic Hydrocarbons, and C11 through C22 Aromatic Hydrocarbons, as reported by the Reasonable Confidence Protocol Method for Extractable Petroleum Hydrocarbons.
Extractable Total Petroleum Hydrocarbons	Hydrocarbons which elute within the C9 through C36 range, including aliphatic and aromatic hydrocarbons, as reported by the Reasonable Confidence Protocol Method for Extractable Total Petroleum Hydrocarbons.
Gas Chromatography	An analytical method used to characterize organic compounds. Gas chromatography methods employ a variety of detectors that respond to various classes of organic compounds aiding in determining the specific compound(s) present.
Indicator Compounds	Compounds which are commonly indicative of a specific class of petroleum products.
Oxygenates	Compounds which are added to fuels to increase oxygen content, such as the additive compound ethanol.
Petroleum	Petroleum is used in this document as the term is defined in Section 22a-449a of the Connecticut General Statutes.
Reasonable Confidence Protocols	The Reasonable Confidence Protocols are analytical methods that include specific laboratory quality assurance and quality control (QA/QC) criteria that produce analytical data of known and documented quality. The Reasonable Confidence Protocols methods are published on the DEEP website at: http://www.ct.gov/deep/cwp/view.asp?a=2715&q=324958&deepNav_GID=16206.
Release	"Release" means any discharge, spillage, uncontrolled loss, seepage, filtration, leakage, injection, escape, dumping, pumping, pouring, emitting, emptying, or

	disposal of a substance, as defined in Remediation Standard Regulations, Section 22a-133k-1(a) of the RCSA.
Reporting Limit	Reporting limit means the concentration of the lowest calibration standard of a calibration curve used for analysis of a given sample by a specific method, corrected for specific sample weight or volume, dilutions, and for soil and sediment samples moisture content.
Target Analytes	Target analytes are the compounds included on the list of analytes for an analytical method.
Volatile Petroleum Hydrocarbons	Volatile Petroleum Hydrocarbons (VPH) are defined as collective fractions of hydrocarbon compounds eluting from n-pentane to naphthalene, excluding Target VPH Analytes. VPH is comprised of C5 through C8 Aliphatic Hydrocarbons, C9 through C12 Aliphatic Hydrocarbons, and C9 through C10 Aromatic Hydrocarbons, as reported by the Reasonable Confidence Protocol Method for Volatile Petroleum Hydrocarbons.

1. INTRODUCTION

The purpose of this document is to provide information to assist the environmental professional in the selection of appropriate analytical method(s) to characterize petroleum releases. Releases of these types are the most commonly investigated by environmental professionals. For example, in Connecticut, for the year 2008 at least 55 percent of all releases reported to the Department of Energy and Environmental Protection's (DEEP) Oil and Chemical Spill Response Division were petroleum releases. In addition, over 95 percent of all underground storage tank releases in Connecticut in 2008 were petroleum products.

Petroleum products:

- Include fuels, biofuels, some synthetic oils and naturally occurring hydrocarbons;
- Are highly variable mixtures resulting in different physical, chemical, and toxicological properties based on the substances present; and
- May also include additives.

The Remediation Standard Regulations (RSRs) as originally promulgated in 1996 focused on the identification of specific indicator compounds, such as benzene, toluene, ethyl benzene, xylenes, and/or the quantitation of a "Total Petroleum Hydrocarbon" (TPH) concentration for the evaluation of a release associated with petroleum products. Since the time the RSRs were promulgated additional methods were developed and have been used to characterize petroleum releases. These methods include:

- Extractable Total Petroleum Hydrocarbon Method (ETPH);
- Extractable Petroleum Hydrocarbon Method (EPH);
- Volatile Petroleum Hydrocarbon Method (VPH); and
- Air-Phase Petroleum Hydrocarbons Method (APH).

Guidance to assist the environmental professional in the selection of appropriate analytical methods to fully characterize petroleum releases is presented in the remainder of this document.

2. SUGGESTED ANALYTICAL METHODS FOR EVALUATION OF PETROLEUM RELEASES

It is the responsibility of the environmental professional to select appropriate analytical methods based on the nature of the release, site history, and the capability of the analytical methods to detect and adequately evaluate the known or potential releases at a site. As needed, the environmental professional should obtain peer review of decision making or consult with knowledgeable experts for advice on topics outside their area of expertise.

Method selection should take into consideration the expected constituents of concern associated with the release for which analysis is being conducted as well as transformations of contaminants that might occur over time or in response to geochemical changes in the subsurface.

Figure 1 illustrates the carbon ranges for various petroleum products. This figure also illustrates the carbon ranges included in analytical methods which are described in this document. This information is provided to help the environmental professional select the appropriate analytical method to characterize a release. General information and a comparison of analytical methods are presented in Appendices A and B.

Suggested analytical methods for various types of releases are described for Soil, Sediment and Aqueous Matrices on Table 1 and for Air and Soil Vapor on Table 2.

The criteria in Appendices A through F of the Remediation Standard Regulations (RSRs), sections 22a-133k-1 through 22a-133k-3 of the Regulations of Connecticut State Agencies (RSCA) are used to determine if a potential risk to human health or the environment may exist. The results of analyses performed on environmental media are used to determine if remediation is needed based on comparison to these criteria.

All analytical measurements have some level of uncertainty. Because of the nature of environmental media, limitations of analytical methods, characteristics of analytes, and human error, the results of environmental analysis may contain a greater level an element of uncertainty and in some cases may be significantly biased, and therefore may not be representative of the actual concentrations of the analytes in the environmental media. Accordingly, the environmental professional should review data to gain an understanding of representativeness.

This is also important since different analytical methods may produce several results for the same analyte. For example, benzene is reported by Method 8260 as well as a target analyte by the VPH Method. Similarly, naphthalene is a target analyte of Method 8260, Method 8270, VPH, and EPH. In general, GC/MS methods

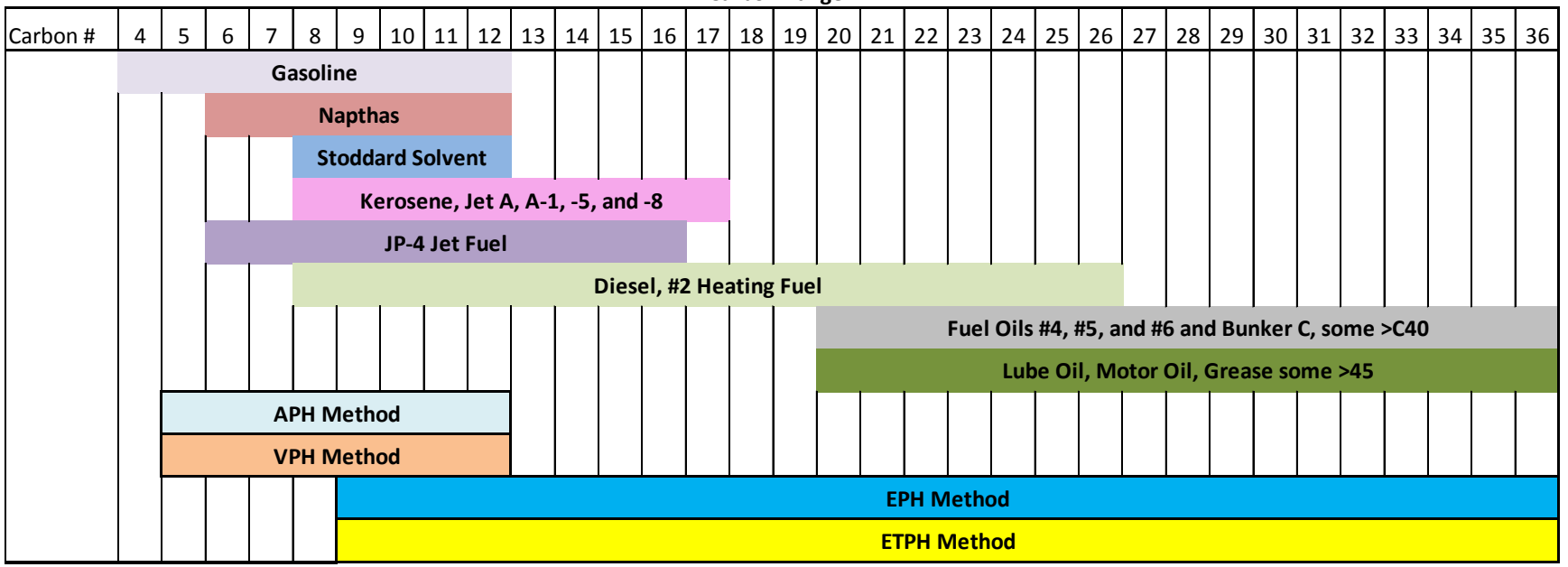
are preferred for target analytes when results for the same compound exist. Nevertheless, DEEP suggests that environmental professionals review QC data for each result.

In addition, analytical methods may analyze for different analytes or different suites of analytes. For example, EPA Method 8260 analyzes for specific compounds only, while the VPH method analyzes for specific target analytes (which are a subset of the compounds reported by the EPA 8260 Method) and also analyzes for defined carbon ranges that are not reported by the EPA 8260 Method. For example, groundwater samples were collected and were analyzed by EPA Method 8260 and the VPH method. The EPA Method 8260 results show concentrations less than the groundwater protection criteria and samples results from the VPH method show concentrations of several carbon ranges greater than the groundwater protection criteria.

EPA Method 8260 results should not be used to ignore or trump VPH Method carbon range results. This is because petroleum releases are made up of a complex mixture of petroleum hydrocarbons. The VPH Method evaluates petroleum hydrocarbons by reporting the results for specific carbon ranges and target compounds found in petroleum hydrocarbons. The EPA 8260 Method does not measure all of the compounds present in the hydrocarbon ranges measured by the VPH Method, but rather reports the results of a list of target compounds. Because of the differences in the results produced by these methods, the 8260 results are not directly comparable to the VPH Method results and may be less representative of the release.

If the environmental professional has reason to believe that an analytical method or suite of analytical methods characterizes the release better than another, and as long as all data obtained are considered, then they will have to explain the results of that option and thoroughly document the rationale for the reasoning in the reports that use the data.

Figure 1
Carbon Range*



Notes:

*Carbon ranges can vary
Reference for carbon ranges - Volume 1, Analysis of Petroleum Hydrocarbons in Environmental Media, Total Petroleum Criteria Workgroup Series, pages 61-68
Analytical carbon ranges from the Reasonable Confidence Protocol for each method

Table 1

Suggested Analytical Methods for Evaluation of Petroleum Releases in Soil, Sediment and Aqueous Matrices[1]

Petroleum Product Released	Analytical Methods for Release Characterization	Comments
Gasoline	8260 Or[2] VPH (carbon ranges and target compounds) Or[2] VPH (carbon ranges only) and 8260	Consider analysis for the following oxygenates/additives on a site-specific basis: ethanol, tert-butyl alcohol, ethyl-tert-butyl-ether, tert-amyl methyl ether, 1,2- dichloroethane, diisopropyl ether, lead and other fuel additives such as ethylene dibromide (EDB) based on the conceptual site model. If the spill is potentially impacting a water supply or is located in a GA/GAA area, conduct analysis for volatile organic compounds (VOCs) using EPA Method 524.2/3 or the low-level RCP Method 8260. Samples from water supply wells should be analyzed for VOCs using EPA Method 524.2/3 which is a drinking water method.
Light Petroleum Solvents (naphtha, Stoddard Solvent, mineral spirits, paint thinner, etc.)	ETPH and 8260 Or[2] VPH (carbon ranges and target compounds)	If the spill is potentially impacting a water supply or is located in a GA/GAA area, conduct analysis for VOCs using EPA Method 524.2/3 or low-level RCP Method 8260. Samples from water supply wells should be analyzed for VOCs using EPA Method 524.2/3 which is a drinking water method.
Jet Fuels and Kerosene	8260, 8270 PAHs, and ETPH Or[2] VPH (carbon ranges and target compounds), ETPH and 8270 PAH's Or[2] VPH and EPH (carbon ranges and target compounds for each method)	If the spill is potentially impacting a water supply or is located in a GA/GAA area, conduct analysis for VOCs using EPA Method 524.2/3 and or low-level RCP Method 8260 and SVOCs using EPA Method 525.2 and or low-level RCP Method 8270. Samples from water supply wells should be analyzed for VOCs using EPA Method 524.2/3 and SVOCs using EPA Method 525.2 which are drinking water methods. It may be appropriate to analyze for the entire target analyte list in EPA Method 8270 list.

#2 Fuel Oil, Diesel	ETPH, 8260, and 8270 PAH's Or[2] EPH and VPH (carbon ranges and target compounds for each method)	If the spill is potentially impacting a water supply or is located in a GA/GAA area, conduct analysis for VOCs using EPA Method 524.2/3 or low-level RCP Method 8260. Samples from water supply wells should be analyzed for VOCs using EPA Method 524.2/3 and SVOCs using EPA Method 525.2 which are drinking water methods. It may be appropriate to analyze for the entire target analyte list in EPA Method 8270 list. Metals[3]
#3 - #6 Fuel Oils, Lubricating Oils, and Hydraulic Oils	ETPH and 8270 PAH's Or[2] EPH (carbon ranges and target compounds)	Samples from water supply wells should be analyzed for SVOCs using EPA Method 525.2 is a drinking water methods. It may be appropriate to analyze for the entire target analyte list in EPA Method 8270/525.2 list. Metals[3]
Waste Oils, Used Oils and Unknown Petroleum Substances	8260, 8270, EPH (or ETPH), VPH, metals, and PCBs by 8082 (carbon ranges only for VPH/EPH)	Full target list of 8270 (acids and base/ neutrals) Consider analysis for the following oxygenates/additives on a site-specific basis: ethanol, tert-butyl alcohol, ethyl-tert-butyl-ether, tert-amyl methyl ether, di-isopropyl ether, lead and other fuel additives such as EDB based on the conceptual site model. Samples from water supply wells should be analyzed for VOCs using EPA Method 524.2/3 and SVOCs using EPA Method 525.2 which are drinking water methods. PCBs are qualitatively identified as Aroclors and measured for compliance purposes as decachlorobiphenyl. Users of Method 505 may have more difficulty achieving the required detection limits than users of Methods 508.1, 525.2 or 508. If the spill is potentially impacting a water supply or in a GA/GAA area, conduct analysis for VOCs using EPA Method 524.2/3 or low-level RCP Method 8260. Samples from water supply wells should be analyzed for VOCs using EPA Method 524.2/3 and SVOCs using EPA Method 525.2 which are drinking water methods. Determine metals selected for analysis on a site-specific basis.

Transformer Oils, Mineral Oils and Dielectric Fluids	EPH (carbon ranges and target compounds) and PCBs by 8082 Or[2] ETPH, 8270, and PCBs by 8082	It may be appropriate to analyze a subset of the EPA Method 8270 list (e.g., PAHs). Samples from water supply wells should be analyzed for SVOCs using EPA Method 525.2 is a drinking water methods. PCBs are qualitatively identified as Aroclors and measured for compliance purposes as decachlorobiphenyl. Users of Method 505 may have more difficulty achieving the required detection limits than users of Methods 508.1, 525.2 or 508.

Notes:

1 - See information regarding sampling and analytical methods for Underground Storage Tank Closure.

2 – The word "or" is used to present acceptable alternative analytical approaches which may be used. It is important to note that some analytical methods may analyze for different analytes or suites of constituents that are not reported by another analytical method. Therefore, the environmental professional should recognize that the results from the alternative analytical approaches may not be comparable or interchangeable.

3 – Include testing for metals based on the conceptual site model; include metals worn off during manufacturing processes.

Definitions:

505 EPA Method 505 for determination of organohalide pesticides and commercial polychlorinated biphenyls (PCBs)

508 EPA Method 508.1 for determination of chlorinated pesticides

508.1 EPA Method 508.1 for determination of chlorinated pesticides, herbicides, and organohalides

524.2/3 EPA Method 524.2 for determination of volatile organic compounds in drinking water

525.2 EPA Method 525.2 for determination of semivolatile organic compounds in drinking water

8082 EPA SW-846 Method 8082 for determination of polychlorinated biphenyls (PCBs)

8260 EPA SW-846 Method 8260 for determination of volatile organic compounds

8270 EPA SW-846 Method 8270 for determination of semivolatile organic compounds

EPH Extractable Petroleum Hydrocarbons – an analytical method to evaluate concentrations of three specific hydrocarbon fractions within the overall hydrocarbon range of C9 to C36. The methodology is described in the "Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements, EPH by the Massachusetts DEP EPH Method," published by the DEEP. An alternative method may also be used to identify EPH if approved by the Commissioner.

ETPH Extractable Total Petroleum Hydrocarbons – an analytical method that provides a total concentration of petroleum hydrocarbons in the C9 to C36 range, but does not distinguish specific hydrocarbon fractions within that range. The analytical method is described in the document entitled, "Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements for ETPH by the DPH ETPH Method," which is published by the DEEP.

PCBs Polychlorinated biphenyls

RCP Reasonable Confidence Protocol

VPH Volatile Petroleum Hydrocarbons - an analytical method to evaluate concentrations of three specific hydrocarbon fractions within the overall hydrocarbon range of C5 to C12. The methodology is described in a document entitled, "Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements, VPH by the Massachusetts DEP VPH Method," that is published by the DEEP. An alternative method may also be used to identify VPH if approved by the Commissioner.

Table 2

Suggested Analytical Methods for Evaluation of Petroleum Releases in Air and Soil Vapor[1]

Petroleum Product Released	Analytical Methods for Release Characterization	Comments
Gasoline	APH (carbon ranges and target compounds) Or[2] TO-15 Or[2] TO-17	Consider analysis for the following oxygenates/additives on a site-specific basis: ethanol, tert-butyl alcohol, ethyl-tert-butyl-ether, tert-amyl methyl ether, 1,2- dichloroethane, diisopropyl ether, and other fuel additives such as ethylene dibromide (EDB) based on the conceptual site model. For the APH Method use silica-lined canisters to improve recovery
Light Petroleum Solvents (naphtha, Stoddard Solvent, mineral spirits, paint thinner, etc.)	APH (carbon ranges and target compounds) Or[2] TO-15 Or[2] TO-17	For the APH Method use silica-lined canisters to improve recovery
Jet Fuels, Kerosene	APH (carbon ranges and target compounds) Or[2] TO-15 Or[2] TO-17	For the APH Method use silica-lined canisters to improve recovery
#2 Fuel Oil, Diesel	APH (carbon ranges and target compounds)	For the APH Method use silica-lined canisters to improve recovery
#3 - #6 Fuel Oils, Lubricating Oils, and Hydraulic Oils	(not applicable)	These "heavier" materials exhibit low vapor pressures and may not be measured by the APH method. However, APH should be considered when petroleum contamination may contain naphthalene in addition to any other site specific contaminants.
Waste Oils, Used Oils, and Unknown Petroleum Substances	Consider analysis for the following: APH (carbon ranges and target compounds), TO-10A, TO-15, TO-17, TO-13, and/or oxygenates/additives on a site-specific basis.	If the conceptual site model suggests that non-petroleum compounds may have been released with petroleum products, analysis for those compounds in air should be considered. Use of the TO-17 analysis is appropriate for the screening of petroleum releases. Due to limitations of the sorbent material utilized by the method, analytical data resulting from a TO-17 analysis is not considered representative when demonstrating compliance with the Remediation Standard Regulations.
Transformer Oils, Mineral Oils and Dielectric Fluids	(not applicable)	Although these "heavier" materials exhibit very low vapor pressures, Method TO-10A and TO-13 may be considered on a site-specific basis.

Notes:

1 - See information regarding sampling and analytical methods for Underground Storage Tank Closure.

2 – The word “or” is used to present acceptable alternative analytical approaches which may be used. It is important to note that some analytical methods may analyze for different analytes or suites of constituents that are not reported by another analytical method. Therefore, the environmental professional should recognize that the results from the alternative analytical approaches may not be comparable or interchangeable.

Definitions:

APH	Massachusetts APH Method
TO-10A	Method TO-13A for determination of pesticides and polychlorinated biphenyls
TO-13	Method TO-13A for determination of polycyclic aromatic hydrocarbons
TO-15	Method TO-15 for determination of volatile organic compounds
TO-17	Method TO-17 for determination of volatile organic compounds
RCP	Reasonable Confidence Protocol

3. ANALYTICAL METHODS

The following subsections provide basic information on key analytical methods that are applicable to the analysis of petroleum hydrocarbons, particularly those identified in Tables 1 and Table 2. A list of references is also included in this document.

3.1 Analytical Methods

3.1.1 Extractable Total Petroleum Hydrocarbons

The ETPH Method measures the C9 to C36 range of hydrocarbons, which includes the major components of a number of widely used petroleum products, as presented in Table 1. Because this method does not measure the lighter petroleum compounds, it 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 of the analytical range (C9 through C36 aliphatic and aromatic ranges) of the ETPH Method.

On June 22, 1999, the Commissioner of the State of Connecticut Department of Public Health (DPH) approved an analytical method for determination of ETPH. The method is titled "Analysis of Extractable Total Petroleum Hydrocarbons (ETPH Method) Using Methylene Chloride Gas Chromatograph/Flame Ionization Detection," prepared by the Environmental Research Institute, University of Connecticut, dated March 1999.

3.1.1.1 *ETPH Reporting Limit*

DEEP, in consultation with the Connecticut Department of Public Health, evaluated the reporting limit for the ETPH Method. As a result of this evaluation, the Ground Water Protection Criterion for ETPH, as determined by the ETPH Method was set at 250 micrograms per liter (µg/L), as indicated in the RSRs (as amended June 27, 2013).

Using a reporting limit of 100 µg/L for aqueous samples may result in the “noise” resulting in false positives, and some laboratories have experienced difficulty quantifying ETPH at 100 µg/L and have requested that the reporting limit for the ETPH Method be raised. DEEP recommends that environmental laboratories performing this method should consider raising their reporting limit for aqueous samples to a concentration above 100 µg/L, but equal to or less than 250 µg/L. However, laboratories should still be able to demonstrate the capability of quantifying at the lowest concentration possible above the instrument signal to noise level through the performance of annual method detection limit (MDL) studies.

Laboratories can implement this change when they are ready to do so. Reporting limits are not to be artificially raised by the laboratory. It is never appropriate for an environmental professional to request that the laboratory raise a reporting limit.

ETPH reported present in a sample collected from a drinking water supply well at any concentration may be a potential concern and may necessitate further evaluation, such as additional sampling, more definitive analytical testing or identification of sources and, as determined necessary, mitigation and water treatment. Furthermore, if ETPH is reported at any concentration in a sample collected from a drinking water supply well, it may be considered a polluting substance and the requirements of the Significant Hazard Program section 22a-6u of the Connecticut General Statutes must be evaluated to determine if a Significant Hazard Condition Notification is required. Information regarding the Significant Hazard Program can be found on the DEEP webpage, Significant Environmental Hazard Program. Please contact the Remediation District Supervisor or the Connecticut Department of Public Health for further guidance on this issue.

3.1.2 Extractable Petroleum Hydrocarbons

Petroleum products suitable for evaluation by this method are identified in Table 1.

The EPH Method evaluates petroleum hydrocarbons by reporting the results for specific carbon ranges and target compounds found in petroleum hydrocarbons. The EPH method produces results which allow for cleanups to be based on the risk of the substances present. This method will promote more appropriate risk management, where a spill from a vegetable oil release (less toxic, less risk) is not treated the same as a waste oil spill (more toxic, more risk).

The EPH Method identifies and measures:

- Extractable aliphatic hydrocarbons within two specific ranges: C9 through C18, and C19 through C36;
- Extractable aromatic hydrocarbons within the C11 through C22 range; and
- Target polycyclic aromatic hydrocarbons (PAH) analytes (the list is comprised of seventeen (17) PAH Analytes, four (4) of which are required for the evaluation of diesel fuel releases).

Table 3

EPH Target Polycyclic Aromatic Hydrocarbons (PAH) Analytes

Diesel	**Other Target PAH Analytes**
Naphthalene	Fluorene
2-Methylnaphthalene	Acenaphthylene
Phenanthrene	Anthracene
Acenaphthene	Fluoranthene
	Pyrene
	Benzo(a)anthracene
	Chrysene
	Benzo(b)fluoranthene
	Benzo(k)fluoranthene
	Benzo(a)pyrene
	Indeno(1,2,3-cd)pyrene
	Dibenz(a,h)anthracene
	Benzo(g,h,i)perylene

3.1.3 Volatile Petroleum Hydrocarbons

Petroleum products suitable for evaluation by the VPH Method are those identified in Table 1.

Similar to the EPH Method, the VPH Method evaluates petroleum hydrocarbons by reporting the results for specific carbon ranges and target compounds found in petroleum hydrocarbons. The VPH method produces results which allow for cleanups to be based on the risk of the substances present. This method will promote more appropriate risk management, where a spill of mineral spirits (less toxic, less risk) is not treated the same as a gasoline spill (more toxic, more risk).

- The VPH Method identifies and measures:
- Volatile aliphatic hydrocarbons within two specific ranges: C5 through C8, and C9 through C12;
- Volatile aromatic hydrocarbons are collectively within the C9 to C10 range; and
- Target analytes: benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl-tert-butyl ether (MTBE).

3.1.4 Air-Phase Petroleum Hydrocarbons

Petroleum products suitable for evaluation by the APH Method are those identified in Table 2.

The Air-Phase Petroleum Hydrocarbon (APH) Method is designed to measure the gaseous-phase concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in indoor air and soil vapor. This method will promote more appropriate risk management, where a less toxic spill with less risk, is not treated the same as a more toxic spill.

The APH Method identifies and measures:

- Volatile aliphatic hydrocarbons within two specific ranges: C5 through C8, and C9 through C12
- Volatile aromatic hydrocarbons are collectively quantified within the C9 to C10 range.
- Target APH analytes: 1,3-butadiene, MTBE, benzene, toluene, ethylbenzene, m- & p-xylene, o-xylene, and naphthalene.

3.1.5 GC/MS Methods for VOCs (Methods 8260, 524.2 and 524.3)

These methods are purge and trap gas chromatography/mass spectrometry methods used to determine volatile organic compounds (VOCs) in a variety of matrices including waters, soils, sediments, wastes, etc. For petroleum releases, they provide compound specific information which can be used to develop clean up criteria based on the substances present. The details of these methods can be found on the Quality Assurance and Quality Control webpage.

3.1.6 GC/MS Methods for SVOCs (Method 8270)

Method 8270 is a gas chromatography/mass spectrometry procedure used to determine semivolatile organic compounds (SVOCs) in a variety of matrices including waters, soils, sediments, wastes, etc. For petroleum releases, it provides concentration data for individual PAHs and other compounds which can be used for risk based analyses. The details of this method can be found on the Quality Assurance and Quality Control webpage.

Should low-level quantitation be needed for PAHs, this method can be run in Selective Ion Monitoring (SIM) mode to achieve lower reporting levels.

For enhanced site characterization after initial characterization has been completed, Method 8270 may also be modified to determine alkylated PAHs and biomarkers such as stearanes and triterpanes to aid in qualitative source identification.

3.1.7 GC Methods for PCBs (Method 8082)

Method 8082 is gas chromatography procedure used to determine polychlorinated biphenyls (PCB's), as Aroclors or as individual congeners, in a variety of matrices including waters, soils, sediments, wastes, etc. This method is commonly used to assess waste oil, hydraulic oil and dielectric fluids (transformer oil) for PCBs. The details of this method can be found on the Quality Assurance and Quality Control webpage.

3.1.8 Metals

When designing an analytical plan to characterize a release of metals associated with petroleum products, the environmental professional should consider the substances which may be present based on the site history and select the appropriate analytical methods to detect and characterize a release. Analytical methods for metals can be found on the Quality Assurance and Quality Control webpage.

3.1.9 Vapor Phase Methods

When designing an analytical plan to characterize a release of petroleum products into soil vapor or indoor air, the environmental professional should consider the substances which may be present based on the site history and select the appropriate analytical methods to detect and characterize a release. Analytical methods for vapor samples can be found on the Quality Assurance and Quality Control webpage.

3.1.10 Additives

When considering the appropriate analytical methods to use when characterizing a petroleum release, the environmental professional should consider not only the petroleum hydrocarbons that may have been released but also any additives or other constituents that could have been associated with the petroleum product of interest. The environmental professional should consider the site-specific conceptual model when deciding on the specific analyses that should be conducted for additives, recognizing that there may be gaps in understanding the site history could affect the selection of analyses.

For instance, it is well known that tetramethyl lead, tetraethyl lead, MTBE, and EDB were once used as gasoline additives in the United States. In evaluating whether or not to analyze for these constituents in addition to the petroleum hydrocarbons found in gasoline, the environmental professional should take into consideration the timing of any gasoline releases at the property. A number of potential additives or additional compounds that could be associated with various types of petroleum releases are included in Tables 1 and 2.

Consider analysis for the following oxygenates/additives on a site-specific basis: ethanol, tert-butyl alcohol, ethyl-tert-butyl-ether, tert-amyl methyl ether, 1,2- dichloroethane, diisopropyl ether, lead and other fuel additives such as ethylene dibromide (EDB) based on the conceptual site model. Appropriate methods should be selected in consultation with the laboratory.

4. QUESTION AND ANSWER

4.1 Question 1

How should the age of a release be considered when selecting an analytical suite?

The type of release is more important in determining the analytical suite than the age of the release. Because age may change the composition, location, and distribution of the petroleum hydrocarbons in the subsurface, the consideration as to age of the release is important in development of the conceptual site model.

Composition of the hydrocarbon at the time of release is an important factor in selecting the analytical suite, e.g., leaded gasoline, PCBs in oils, etc.

4.2 Question 2

Are there any plans for retiring ETPH as an analytical method that can be used to demonstrate compliance with the RSRs?

ETPH will continue to be an acceptable method into the foreseeable future.

4.3 Question 3

A groundwater plume in a GA area resulting from a Number 2 Heating Oil release was characterized using the ETPH, 8260, and 8270 Methods. The ETPH concentrations exceeded Ground Water Protection Criterion. Since the ETPH Method measures the C9 to C36 range of hydrocarbons as a single result, are there other methods which break down the C9 to C36 carbon range into smaller subsets allowing for risk-based cleanups?

Yes, the EPH method reports the C9 to C36 carbon range into three carbon ranges, each range with its own criteria. This allows for a more detailed level of risk evaluation. This method will promote more appropriate risk management and cleanup.

4.4 Question 4

What analytical methods are most appropriate for characterizing weathered gasoline in soil and groundwater?

This seems like a simple question but it is not. The answer can be approached from a routine method perspective and then from a forensic perspective. What is the goal for the investigation has to be considered. Volatile compounds will be lost due to weathering.

If we're considering routine methods, then most appropriate would be aromatic compounds by EPA Method 8260 and in addition the VPH method. The EPH method would not be appropriate since this method's carbon range is higher than what gasoline would contain (there is a slight overlap but again we are talking about the most appropriate methods).

If we're coming at this from a forensic perspective, then a specialized method called PIANO would be considered but very few labs in the country can do this method at the time of the publication of this document.

4.5 Question 5A

Which analytical suite should be chosen to determine whether there has been a release of residential heating fuel?

DEEP recommends ETPH or alternatively EPH carbon ranges only as an initial characterization method for soil and/or groundwater. DEEP advises that additional information about the release is achieved using EPA Method 8260 (aromatics only) and 8270 (PAHs only) or EPH and VPH (carbon ranges and target compounds for each method).

4.6 Question 5B

After a release of residential heating fuel is confirmed is analysis of soil or water from a potable well necessary?

Yes. DEEP recommends that soil samples collected taken to determine the extent of the release and/or to determine that remediation was effective be analyzed by ETPH or alternatively EPH carbon ranges only. If information is obtained using the additional methods referenced in Question 5A above, and if detections are greater than RSR cleanup criteria (RSRs used as guidance), then samples collected to determine the extent of the release and/or to determine that remediation was effective should also be analyzed by the appropriate methods as needed to address those exceedances.

If there is a potable well(s) present in the area that may be threatened, then it is strongly recommended the potable well(s) be tested using ETPH or EPH carbon ranges only and 524.2/524.3 for VOCs and 525.2 (PAHs only).

4.7 Question 6

Should I use EPA Method 8260 or EPA Method 524.2/3 to test ground water in a GA Groundwater Classification Area?

The Connecticut Remediation Standard Regulations require drinking water methods be used to analyze certain ground water samples collected from a GA area. The low-level modification to the Connecticut DEEP Recommended Protocol for Method 8260 may be used in place of Method 524.2 for purposes of compliance with the RSRs with the approval of the Connecticut DEEP.

However, water samples from drinking water wells need to be tested by drinking water methods established in subpart C of 40 CFR part 141, such as Method 524.2/3 (VOCs) or Method 525 (SVOCs).

4.8 Question 7

Are the EPH and VPH methods capable of achieving reporting limits which are equal or less than applicable RSR criteria for target compounds?

Yes, the VPH method can achieve sensitive enough reporting limits for target compounds in both soil and water without method modification. The EPH method can achieve sensitive enough reporting limits for target compounds in soil without method modification. Method modification or alternate methods such as EPA Method 8270 SIM for PAHs are needed to achieve sensitive enough reporting limits for target compounds in water.

On occasion, a particular sample may present issues in achieving desired reporting limits for target compounds using the EPH or VPH methods. In those cases EPA Methods 8270 or 8260 may be better choices to achieve the desired reporting limits for target compounds. Consult with your lab to decide the best course of action.

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