Extractable Petroleum Hydrocarbon Fractions Using the ETPH Analytical Method and Criteria Development

TECHNICAL SUPPORT DOCUMENT

Connecticut Department of Energy and Environmental Protection
Connecticut Department of Public Health
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Contents

List of Tables

Background and Analytical Considerations

The Connecticut Remediation Standard Regulations, Sections 22a-133k-1 through 22a-133k-3 of the Regulations of Connecticut State Agencies (RSRs), contain environmental criteria to facilitate the assessment and remediation, as necessary, at sites within Connecticut which have been affected by releases of various substances. Within the regulations promulgated in 1996, criteria were established for certain individual semi-volatile substances commonly associated with releases of petroleum hydrocarbon mixtures in addition to criteria for Total Petroleum Hydrocarbons (TPH) as a complex aggregate of substances as reported by the United States Environmental Protection Agency (EPA) Method 418.1, which utilized Freon-111. In an effort to help bring about the end of Freon use in Connecticut and to be consistent with Federal Law, the Connecticut Department of Energy and Environmental Protection (DEEP) stopped accepting analytical data derived by EPA Method 418.1 for samples collected on or after June 30, 2009. In addition, the Environmental Laboratory Certification Program of the Connecticut Department of Public Health stopped offering certification for EPA Method 418.1 as of September 30, 2009 and after this deadline laboratories may not use EPA Method 418.1. Since the TPH remediation criteria in the regulations were method specific, and laboratories could no longer use EPA Method 418.1, this effectively prevented the use of the promulgated criteria from use at remediation sites for samples collected on or after June 30, 2009.

Since 1999, another analytical method has been available for use in Connecticut to evaluate petroleum hydrocarbons as a complex mixture of aggregate of substances. This method is titled "Analysis of Extractable Total Petroleum Hydrocarbons Using Methylene Chloride Gas Chromatograph/Flame Ionization Detection (ETPH Method)," prepared by the Environmental Research Institute, University of Connecticut, dated March 1999 and approved by the Commissioner of the State of Connecticut Department of Public Health (CT DPH) on June 22, 1999. Certain remediation criteria using the ETPH Method were recommended at that time for the Extractable Total Petroleum Hydrocarbons fraction (ETPH) and have been available for use with site-specific approval at remediation sites. The ETPH Method reports ETPH which is different from TPH as reported by EPA Method 418.1

Criteria for petroleum hydrocarbons are developed to complement the analytical methods used to determine the amount of petroleum hydrocarbons present. As petroleum hydrocarbons are a complex aggregate of substances, the results of petroleum hydrocarbon analyses differ depending on the analytical method used, with each method targeting a slightly different subset of the full amount of petroleum hydrocarbons potentially present. DEEP intends to propose a revision of the RSRs to include criteria for the ETPH petroleum hydrocarbon fraction based on the ETPH Method identified in Table 1.

Table 1: Analytical Method for Extractable Total Petroleum Hydrocarbons

Method Name	Method Developed By	Petroleum Hydrocarbon Fractions Analyzed
ETPH Method: Connecticut Extractable Total Petroleum Hydrocarbons Method	Environmental Research Institute, University of Connecticut[1]	The ETPH Method measures the C9 to C36 range of petroleum hydrocarbons which includes the major components of a number of widely used petroleum products such as kerosene, jet and diesel fuels, number 2 to No. 6 fuel oils, and motor oil.

Note 1 - CT Reasonable Confidence Protocols for the ETPH Method available on DEEP Website

Additional guidance on the implementation of this method and criteria into remediation projects and analytical quality assurance guidance will be provided in separate documents, available on the DEEP website as well as in Appendix A to this document.

The ETPH Method is a helpful tool because it allows for quick and inexpensive analysis. The adoption of criteria based on the ETPH Method into the regulations will allow sites with releases of certain petroleum products to have the option to self-implement the use of these criteria. Additionally, following adoption, site-specific criteria for extractable petroleum hydrocarbons may be proposed for use on a case-by-case basis in lieu of using the ETPH based criteria.

In conjunction with the proposed regulatory adoption of these criteria, DEEP is also proposing, in a separate document, guidance regarding recommended remediation criteria based on an alternative analytical methods for extractable, volatile and air-phase petroleum hydrocarbons for use on a case-by-case basis at remediation sites in need of such criteria. These recommended criteria are not proposed for adoption into the RSRs at this time. The recommended additional criteria or other site-specific criteria may be proposed for use on a case-by-case basis.

Extractable Petroleum Hydrocarbon Fractions Using the ETPH Analytical Method and Criteria Development

Remediation criteria for use with the ETPH Method were previously identified by DEEP and included Direct Exposure Criteria, Pollutant Mobility Criteria and Groundwater Protection Criteria. The previously identified values are proposed for adoption without modification at this time in place of updated risk-based values in order to allow for programmatic continuity for projects currently underway.

In addition to these criteria, DEEP is proposing to adopt Groundwater Volatilization Criteria and Surface Water Protection Criteria for the ETPH Method. This will provide for a full complement of remediation criteria for sites with releases of extractable petroleum hydrocarbon fraction. Risk-based criteria for extractable petroleum hydrocarbons using ETPH Method were derived for Groundwater Volatilization Criteria and Surface Water Protection Criteria using information developed during the risk-based evaluation of extractable petroleum hydrocarbon fractions for the Extractable Petroleum Hydrocarbons Method (EPH Method).

Both the ETPH and EPH methods evaluate the amount of petroleum hydrocarbons within a sample. The ETPH analysis yields one value to represent the total amount of extractable petroleum hydrocarbons in the C9 to C36 range of hydrocarbons while the EPH method provides results for three hydrocarbon fractions. As it is possible that the extractable petroleum hydrocarbons within a sample could preferentially occur within one of these three hydrocarbon fractions, the risk-based ETPH Groundwater Volatilization Criteria and Surface Water Protection Criteria have been selected as the lowest risk-based criteria from the three EPH fractions as presented in Petroleum Hydrocarbons Using the EPH/VPH/APH Analytical Methods and Criteria Development. The risk-based criteria were adjusted, as appropriate, to reflect the aqueous reporting limit of 250 ug/L for the ETPH Method. A summary of the criteria derivation is provided in Appendices B and C to this document while additional information can be found in Petroleum Hydrocarbons Using the EPH/VPH/APH Analytical Methods and Criteria Development.

Once the risk-based values were calculated, the resulting value was adjusted to account for achievable analytical levels.

Table 2: Analytical Reporting Levels per CT RCP Method Documents*

Method	Aqueous (ug/l)	Soil (mg/kg)	Air (ug/m^3)
ETPH	250*	100	NA

*Note: Current CT Reasonable Confidence Protocols documents indicate that Reporting Level for Aqueous Solutions for ETPH method is 100 ug /L. Based on recent reports from CT DPH, it is expected that the RCP documents for these methods will be revised to reflect a new reporting limit of 250 ug /l.

Summary of Recommended Criteria Values

The ETPH criteria summarized in Table 3 below are proposed at this time. Unless and until the RSRs are amended to include ETPH criteria, parties may request site-specific approval by DEEP for these criteria as Additional Polluting Substances. Parties may also request approval of different criteria for ETPH as Addition Polluting Substances and would need to submit technical support for such request. If and when ETPH criteria are incorporated into the numeric criteria in the RSRs, they would be self-implementing at such time.

Table 3: Proposed Remediation Criteria for Use with the ETPH Method

Criteria	Units	Value	Basis
Direct Exposure Criteria: Residential	mg/kg	500	Previously proposed value
Direct Exposure Criteria: Industrial/Commercial	mg/kg	2,500	Previously proposed value
Pollutant Mobility Criteria: GA Areas	mg/kg	500	Previously proposed value
Pollutant Mobility Criteria: GB Areas	mg/kg	2,500	Previously proposed value
Groundwater Protection Criteria	ug/l	250	Analytical Adjustment
Surface Water Protection Criteria	ug/l	250	Analytical Adjustment
Groundwater Volatilization Criteria: Residential	ug/l	250	Analytical Adjustment
Groundwater Volatilization Criteria: Industrial/Commercial	ug/l	250	Lowest Fraction from EPH Criteria Derivation

Bibliography

DEEP. 1996. Remediation Standard Regulations. Available at http://www.ct.gov/dep/lib/dep/regulations/22a/22a-133k-1through3.pdf

DEEP. 2003. Connecticut's Proposed Revisions Remediation Standard Regulations Volatilization Criteria. Available at: http://www.ct.gov/dep/lib/dep/site_clean_up/remediation_regulations/RvVolCri.pdf

DEEP. 2006. State Of Connecticut Department of Environmental Protection Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements For Extractable Petroleum Hydrocarbons by the State Of Connecticut, Department of Public Health ETPH Method. Available at: http://www.ct.gov/dep/lib/dep/site_clean_up/guidance/RCP/RCP_Method_ETPH.pdf

DEEP. 2012. Petroleum Hydrocarbons Using the EPH/VPH/APH Analytical Methods and Criteria Development. Available on the DEEP web page about Additional Polluting Substances

APPENDICES

Appendix A
Considerations for Use of Analytical Methods

Use of Leaching Procedures for PMC Compliance Determinations

Restrictions contained in RCSA section 22a-133k-2(c) prohibit the use of the Toxicity Characteristic Leaching Procedure, EPA Method 1311("TCLP") and the Synthetic Precipitation Leaching Procedure, and EPA Method 1312 ("SPLP") for the analysis of Total Petroleum Hydrocarbons ("TPH") by EPA Method 418.1.

The TCLP and SPLP can be used with the ETPH, EPH and VPH methods because these methods do not report TPH using EPA Method 418.1.

Restrictions contained in RCSA section 22a-133k-2(c) prohibit the use of the TCLP and SPLP for the analysis of 1,2 dichlorobenzene, ethyl benzene, toluene and xylenes. These restrictions are proposed to be deleted from the Remediation Standard Regulations RCSA sections 22a-133k-1 through 22a-133k-3, inclusive.

Use of Groundwater Data in Evaluating Pollutant Mobility

Proposed amendments to Section 22a-133k-c(4) Pollutant Mobility Exemptions include the ability to utilize groundwater data, in specific circumstances, to demonstrate compliance with the pollutant mobility requirements when soil leaching analyses produce results that exceed the RSR pollutant mobility criteria.

Appendix B
Volatilization Criteria

Table B-1 Calculation of Residential Groundwater Volatilization Criteria

Chemical Name	Chemical Type	Toxicity Values		Risk-Based Criteria (µg/L)	Ceiling Value (µg/L)	Analytical Reporting Level (µg/L)	Final Criteria (µg/L)	Basis
		Type	mg/kg/d					
C_9-C_{18} EPH Aliphatic	Extractable	RfC - Inhalation	0.2	83.17	50,000	100	100	Analytical Adjustment
C_{19}-C_{36} EPH Aliphatic	Extractable	RfC - Inhalation	Not Volatile		50,000	100		
C_{11}-C_{22} EPH Aromatic	Extractable	RfC - Inhalation	0.025	5,135.56	50,000	100	5,135	Risk-based
ETPH	Extractable			83.17		250	250	Analytical Adjustment

Table B-2 Calculation of Industrial/Commercial Groundwater Volatilization Criteria

Chemical Name	Chemical Type	Toxicity Values		Risk-Based Criteria (µg/L)	Ceiling Value (µg/L)	Analytical Reporting Level (µg/L)	Final Criteria (µg/L)	Basis
		Type	mg/kg/d					
C_9-C_{18} EPH Aliphatic	Extractable	RfC - Inhalation	0.2	255.02	50,000	100	255	Risk-based
C_{19}-C_{36} EPH Aliphatic	Extractable	RfC - Inhalation	NA		50,000	100		
C_{11}-C_{22} EPH Aromatic	Extractable	RfC - Inhalation	0.025	12,014.54	50,000	100	12,000	Risk-based
ETPH	Extractable			255.02		250	255	Risk-based

Appendix C
Surface Water Protection Criteria

Table C-1 Calculation of Surface Water Protection Criteria

Chemical Name	Chemical Type	Surrogate	Chronic Aquatic Life Criteria ug/L	Chronic Aquatic Life Criteria Basis	Risk-Based Surface Water Protection Criteria ug/L	Analytical Reporting Level ug/L	Final Criteria ug/L	Surface Water Protection Criteria Basis
C9-18 EPH Aliphatic	Extractable	Decane	77	CT Tier 2	770	100	770	Risk-based
C19-36 EPH Aliphatic	Extractable	Cyclododecane	53	CT Tier 2	530	100	530	Risk-based
C11-22 EPH Aromatic	Extractable	Acenaphthene Anthracene Fluoranthene Fluorene Phenanthrene Pyrene	Acenaphthene: 15 Anthracene: 0.0253 Fluoranthene: 0.914 Fluorene: 3.23 Phenanthrene: 1.4 Pyrene: 7.78 Average: 4.7	GLI 2.11	47	100	100	Analytical Adjustment
ETPH	Extractable				47	250	250	Analytical Adjustment

GLI 2.11 : Great Lakes Initiative Toxicity Data Clearinghouse V 2.11

Table C-2 Calculation of Connecticut Tier 2 Chronic Aquatic Life Criteria

	Decane	**Cyclododecane**
Lowest Genus Mean Acute Value (ug/L)	18000	21000
Number of Data Requirements Satisfied	2	1
Secondary Acute Factor	13	21.9
Secondary Acute Value (ug/L)	1385	959
Acute to Chronic Ratio	18	18
Acute Aquatic Life Water Quality Criteria (ug/l)	**692**	**479**
Chronic Aquatic Life Water Quality Criteria (ug/l)	**77**	**53**

Table C-3 Data Used to Derive Aquatic Life Criteria for Decane

Derivation of Freshwater Aquatic Life Criteria				
Chemical	**Decane**			
CASRN	124185			
Date of EcoTox Query	August 17, 2011			
Data Requirements: Data from 8 Different Families Including:				
1. Family Salmonidae in the Class Ostreichthyes				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
2. One Other Warm Water Species in Class Ostreichthyes which is Commercially or Recreationally Important				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
Lepomis macrochirus	96 hr LC50	530000	530000	530000
3. Third Family in Phylum Chordata (e.g. fish, amphibian)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
4. Planktonic Crustacean (e.g. cladoceran, copepod)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
Daphnia magna	48 hr EC50	18000	18000	18000
5. Benthic Crustacean (e.g. ostracod, isopod, amphipod)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
6. Insect (e.g. mayfly, dragonfly, stonefly, caddisfly, mosquito, midge)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
7. Family in a phylum other than Arthropoda or Chordata (e.g. Rotifera, Annelida, Mollusca)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
8. Family in Any Order of Insect or Any Phylum not Already Represented				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value

Table C-4 Data Used to Derive Aquatic Life Criteria for Cyclododecane

Derivation of Freshwater Aquatic Life Criteria				
Chemical	**Cyclododecane**			
CASRN	294622			
Date of EcoTox Query	August 17, 2011			
Data Requirements: Data from 8 Different Families Including:				
1. Family Salmonidae in the Class Ostreichthyes				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
2. One Other Warm Water Species in Class Ostreichthyes which is Commercially or Recreationally Important				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
3. Third Family in Phylum Chordata (e.g. fish, amphibian)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
4. Planktonic Crustacean (e.g. cladoceran, copepod)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
Daphnia pulex	48 hr EC50	21000	21000	21000
5. Benthic Crustacean (e.g. ostracod, isopod, amphipod)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
6. Insect (e.g. mayfly, dragonfly, stonefly, caddisfly, mosquito, midge)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
7. Family in a phylum other than Arthropoda or Chordata (e.g. Rotifera, Annelida, Mollusca)				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value
8. Family in Any Order of Insect or Any Phylum not Already Represented				
Organism	Test Type	Result (ug/L)	Species Mean Acute Value	Genus Mean Acute Value