

TNI Environmental Measurement Symposium
Garden Grove, California
August 6th, 2024

The measurement of C₁₉-C₃₆ aliphatic hydrocarbons at a sediment Superfund site using the MADEP Extractable Petroleum Hydrocarbon (EPH) method:
Considerations for data quality and usability

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Introduction

- The Massachusetts Department of Environmental Protection (MADEP) Extractable Petroleum Hydrocarbon Method (EPH) is being used to measure C₁₉-C₃₆ Aliphatics at a sediment superfund site (SFS) in New York.
- The EPH method has been validated by MADEP for use in soil and groundwater analysis but not for use in sediments (MADEP, 2019).
- This presentation reports the results of a method detection limit (MDL) study that assesses the sensitivity, accuracy and precision of the MADEP EPH method for use in measuring complex mixtures of aliphatic hydrocarbons in contaminated sediments.

Site Background

- The SFS is an urban, industrialized, tidally influenced creek in New York.
- During the Remedial Investigation (RI), the MADEP EPH method was used to measure C₁₉-C₃₆ Aliphatic hydrocarbons in complex sediments, although C₁₉-C₃₆ Aliphatics was not initially identified as a contaminant of concern (COC).
- Following a supplemental review of toxicity data after the baseline ecological risk assessment (BERA) was completed, the EPA set a risk-based preliminary remediation goal (PRG) for C₁₉-C₃₆ Aliphatics of 200 mg/kg.
- In further reviewing the site sediment data, stakeholders observed indications of C₁₉-C₃₆ Aliphatic data variability at concentrations near the risk-based PRG.
- This prompted stakeholders to initiate an MDL verification study to assess the reliability of the MADEP EPH method in measuring C₁₉-C₃₆ Aliphatics in sediments at concentrations near the risk-based PRG.

EPH Method Sediment Analysis

METHOD FOR THE DETERMINATION OF
EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

Massachusetts Department of Environmental Protection

Bureau of Waste Site Cleanup

Commonwealth of Massachusetts

Executive Office of Energy and Environmental Affairs
Kathleen A. Theoharides
Secretary

Department of Environmental Protection
Martin Suuberg
Commissioner

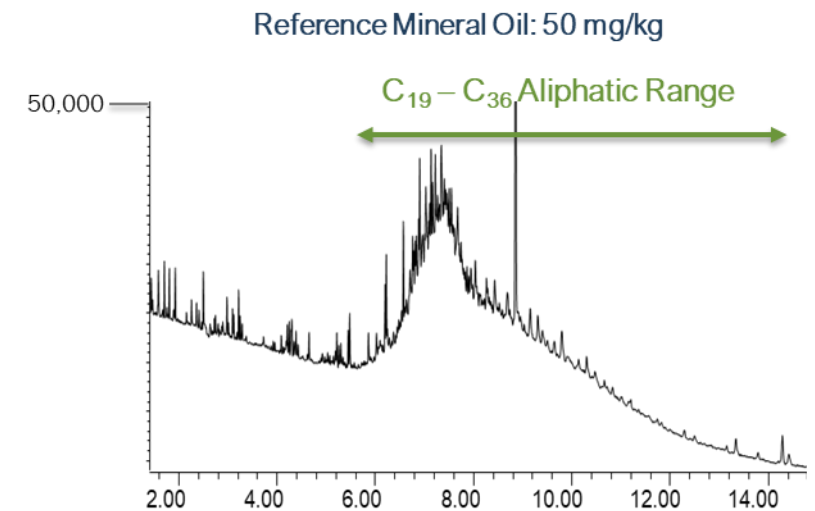
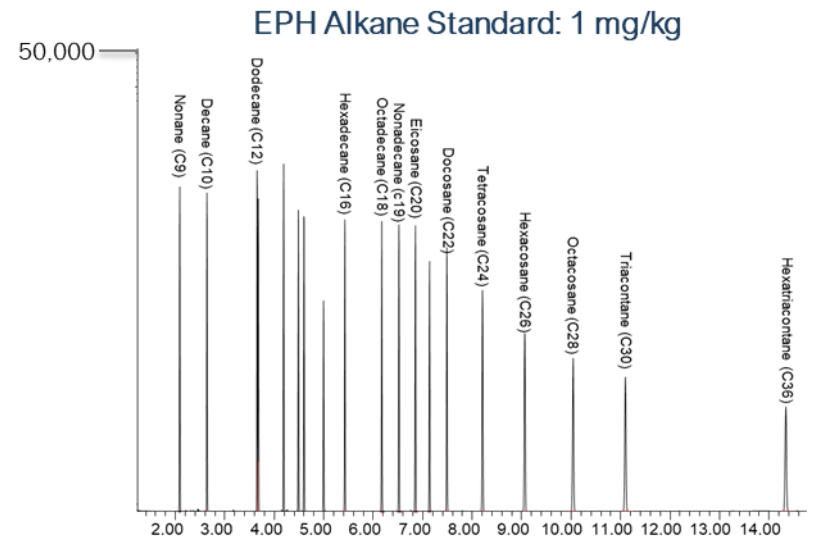
December 2019
Revision 2.1

- MADEP states that the EPH method, “is suitable for the analysis of aqueous samples, soils, sediments, wastes, sludges, and nonaqueous phase liquid (NAPL) samples. However, it should be noted that the method was validated only for soil and aqueous matrices” (MADEP, 2019).
- The SFS C₁₉-C₃₆ Aliphatic sediment risk-based PRG is 200 mg/kg (0.02 % petroleum).
- Sediment matrices “can present unique analytical chemistry challenges such as elevated sediment moisture levels, which directly impact analytical reporting limits (RLs) and analyte extraction efficiencies” (ASTM E3163).
- “Also, sediments may contain elevated concentrations of target or nontarget compounds (or both) and other matrix interferences, necessitating a customized analytical approach to improve data quality and usability outcomes” (ASTM E3163).

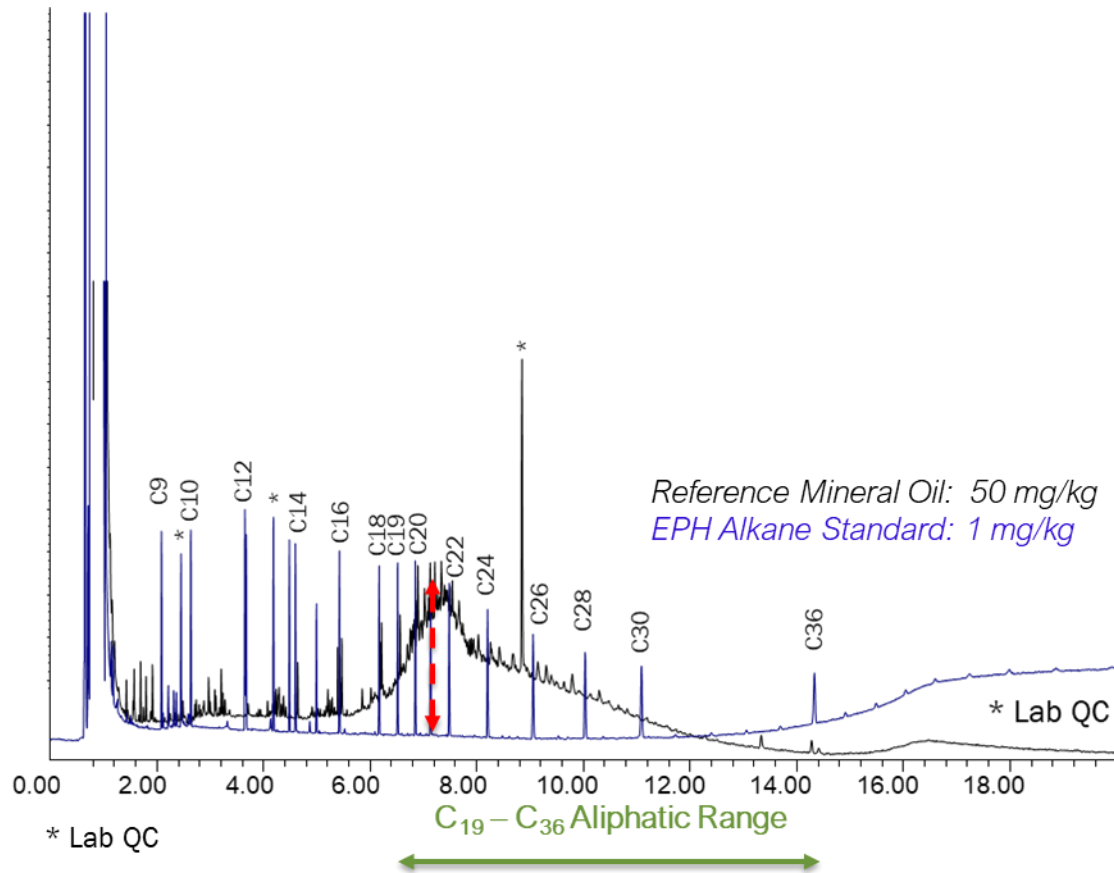
EPH Method Limitations

In addition to matrix considerations, the EPH method has known vulnerabilities that pose challenges to data quality and reliability, especially at low concentrations.

- 1) MDL Sensitivity: Labs commonly perform EPH MDL studies using a clean lab matrix like sodium sulfate and discrete *n*-alkane standards. This approach, although allowed by the method, does not accurately represent the sensitivity of the method when analyzing complex hydrocarbon mixtures in sediments.
- 2) Column Bleed is an instrument artifact and introduces an interference (i.e. positive bias) in the C₁₉-C₃₆ carbon range (ITRC, 2018).
- 3) Manual Range Integration Techniques can vary by analyst and laboratory and if not carefully controlled can introduce variability into results.



Limitations of Methodology: MDL Sensitivity



- C₁₉-C₃₆ Aliphatic MDLs are commonly generated using 8 discrete *n*-alkane standards in the C₁₉-C₃₆ range and are summed to determine an MDL for this hydrocarbon range.
- The use of *n*-alkanes in MDL studies does not represent true instrument sensitivity because the mass of petroleum hydrocarbons in the C₁₉-C₃₆ range are composed of thousands of different hydrocarbons that are not expressed as individual hydrocarbon peaks.
- In contrast to the strong response of the individual *n*-alkane standards used in the method's calibration, the instrument's response to the same mass of C₁₉-C₃₆ Aliphatics is muted.

MADEP EPH MDL Verification Study

- The purpose of the study was to evaluate the suitability of the MADEP EPH method for low-level analysis of C₁₉-C₃₆ Aliphatics in contaminated sediments.
- The most recent USEPA guidance for determining MDLs was strictly followed (USEPA, 2017),
- 8 spiked replicates, 8 blanks were prepared per MDL study,
- Study conducted using mineral oil of appropriate carbon range and lubricating oil reference standards as opposed to discrete *n*-alkane standards,
- Study was performed in sodium sulfate, a clean marine sediment, and a contaminated SFS sediment,
- Three Phases to MDL Study:
 1. Level of Detection - Instrument Sensitivity
 2. MDL Spiking Study – Sodium Sulfate
 3. MDL Spiking Study – Matrix Specific
- Updated MDLs were then used to develop practical quantitation limits (PQLs)

Phase I: Level of Detection

Phase I: Level of Detection		Lab Stated		Level of Detection Determination		
Analyte	Units	MDL	RL	Test Range	Mineral Oil	Lubricating Oil
C19-C36 Aliphatics	mg/kg	6.67	6.67	20 - 70	25	30

The **level of detection** is the lowest concentration that can be reliably distinguished from zero but is not quantifiable with acceptable accuracy and precision.

The level of detection determination was used to determine the spiking level for the MDL study.

Phase II: MDL Study in Sodium Sulfate

Phase II: MDL Sodium Sulfate		Lab Stated		MDL Sodium Sulfate Spiking Study			
Analyte	Units	MDL	RL	MDL Spike	Blank	Mineral Oil	Lubricating Oil
C19-C36 Aliphatics	mg/kg	6.67	6.67	50	13.2	23.8	18.2

The **MDL** is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

Phase III: MDL Study in Sediment

Phase III MDL: Matrix Specific		MDL Marine Sediment and Site Specific Sediment Results				
Analyte	Units	MDL Spike	Sodium Sulfate Method Blank	Mineral Oil - Marine Sediment	Lube Oil - Marine Sediment	Site Matrix - SFS Sediment
C19-C36 Aliphatics	mg/kg	100	9.3	127	127	249

The **MDL** is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

Recommended MDL range using reference oils:

- MDLs: ~ 127 – 249 mg/kg

Practical Quantitation Limits

Practical Quantitation Limit			PQL (MDL Sodium Sulfate)		PQL (MDL Matrix Specific)		
PQL Limit	Analyte	Units	Mineral Oil	Lubricating Oil	Mineral Oil - Marine Sediment	Lube Oil - Marine Sediment	Site Matrix - SFS Sediment
3x MDL	C19-C36 Aliphatics	mg/kg	71.4	54.6	381	381	747
5x MDL	C19-C36 Aliphatics	mg/kg	119	91.1	635	635	1,245
10x MDL	C19-C36 Aliphatics	mg/kg	238	182	1,270	1,270	2,490

The PQL is the lowest level that can be reliably achieved within specified limits of accuracy and precision during routine laboratory operating conditions (US Federal Register 1987). EPA recommends that PQLs are 5x to 10x the MDL as determined in a clean lab matrix.

- The recommended PQL using reference oils in an ultra clean lab matrix at 10x the MDL ranges from **182 to 238 mg/kg.**

There is no formal regulatory guidance for developing PQLs using matrix specific MDL studies. Based on the complicated nature of sediment matrices, and the limitations of the MADEP EPH methodology, it is reasonable to consider a matrix specific PQL of 3x the matrix specific MDL.

- The recommended PQL using reference oils in actual sediment matrices at 3x the matrix specific MDL ranges from **381 mg/kg to 747 mg/kg.**

Summary of Findings

- The current MADEP EPH methodology has not been thoroughly optimized for use in measuring C₁₉-C₃₆ Aliphatics in contaminated sediments.
- Determining MDLs using reference oils containing complex mixtures of aliphatic hydrocarbons, instead of individual *n*-alkanes, provides a more realistic and reliable measure of method sensitivity, accuracy and precision.
- Performing matrix specific MDL studies provides a project or site-specific measure of method sensitivity, accuracy and precision in relevant environmental matrices.
- CERCLA risk-based PRGs/RGs cannot be less than PQLs.
- The C₁₉-C₃₆ Aliphatic risk-based PRG at this SFS is below (or at) the PQL, indicating the MADEP EPH method is not a suitable analytical method to evaluate C₁₉-C₃₆ Aliphatics at 200 mg/kg in contaminated sediments.



Questions?



References

- 1) ASTM. 2018. ASTM E3163-18 Standard Guide for Selection and Application of Analytical Methods and Procedures Used during Sediment Corrective Action.
- 2) Interstate Technology & Regulatory Council (ITRC). 2018. TPH Risk Evaluation at Petroleum-Contaminated Sites. TPHRisk-1. Washington, D.C.: Interstate Technology & Regulatory Council, TPH Risk Evaluation Team.
- 3) MADEP. 1994. Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter.
- 4) MADEP. 2019. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts Department of Environmental Protection, Revision 2.1. 2019.
- 5) US Federal Register 1987. "40 CFR Parts 141 and 142. National Primary Drinking Water Regulations - Synthetic Organic Chemicals, Monitoring for Unregulated Contaminants, Final Rule"; United States Federal Register, Volume 52, Number 130, Pages 25690-25717.
- 6) US Federal Register 2017. "40 CFR, Title 40. Appendix B to Part 136. Clean Water Act Methods Update Rule for the Analysis of Effluent, Final Rule. Definition and Procedure for the Determination of the Method Detection Limit - Revision 2." United States Federal Register, Volume 82, Number 165, Pages 40939-40941.