



The Bulk Measurement of  $C_8$ - $C_{20}$  Petroleum Hydrocarbons and Polar Petroleum Metabolites in Produced Waters and Petroleum Impacted Groundwater

# Introduction



This presentation introduces a straightforward method to directly measure the bulk concentration of dissolved non-polar petroleum hydrocarbons and petroleum metabolites in *produced waters*, *petroleum impacted groundwaters*, and *sediment porewaters*.



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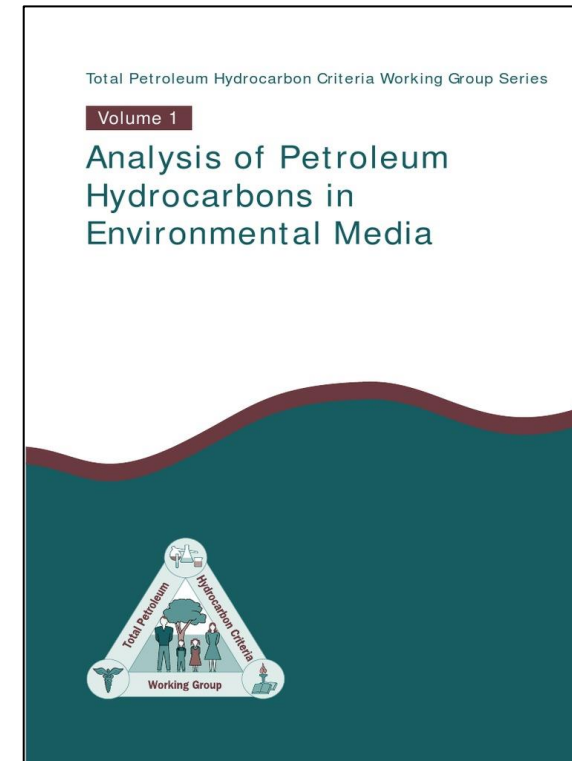
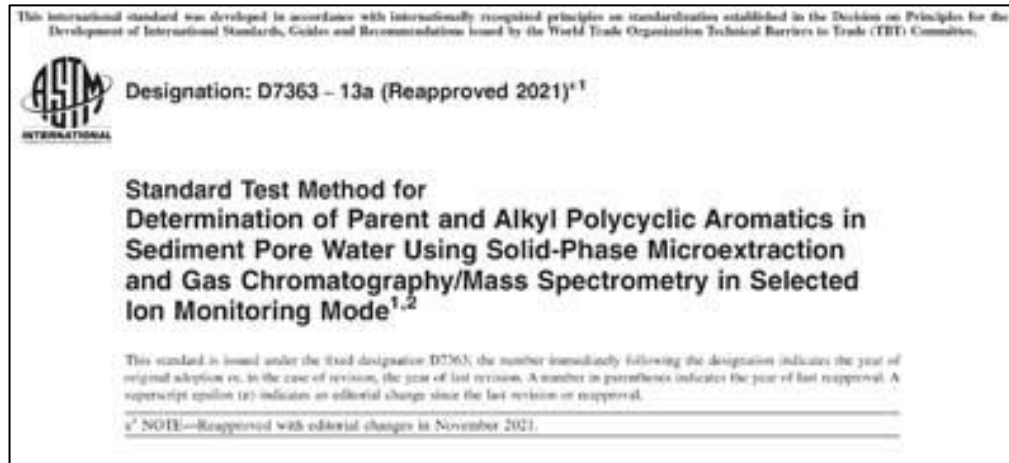


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# Introduction



This method picks up on work done by the TPH Criteria Working Group in applying fraction specific approaches to TPH analysis and relies on existing methods like ASTM D7363 – *Alkylated PAHs in Sediment Porewater*.

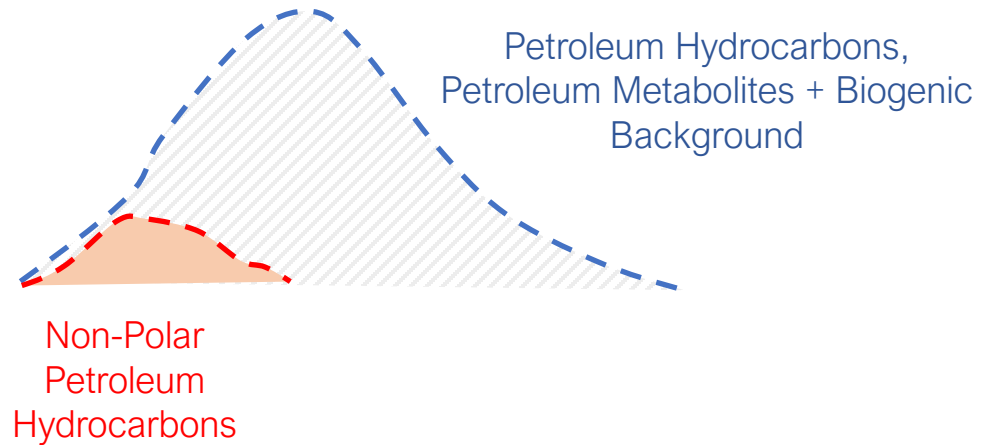
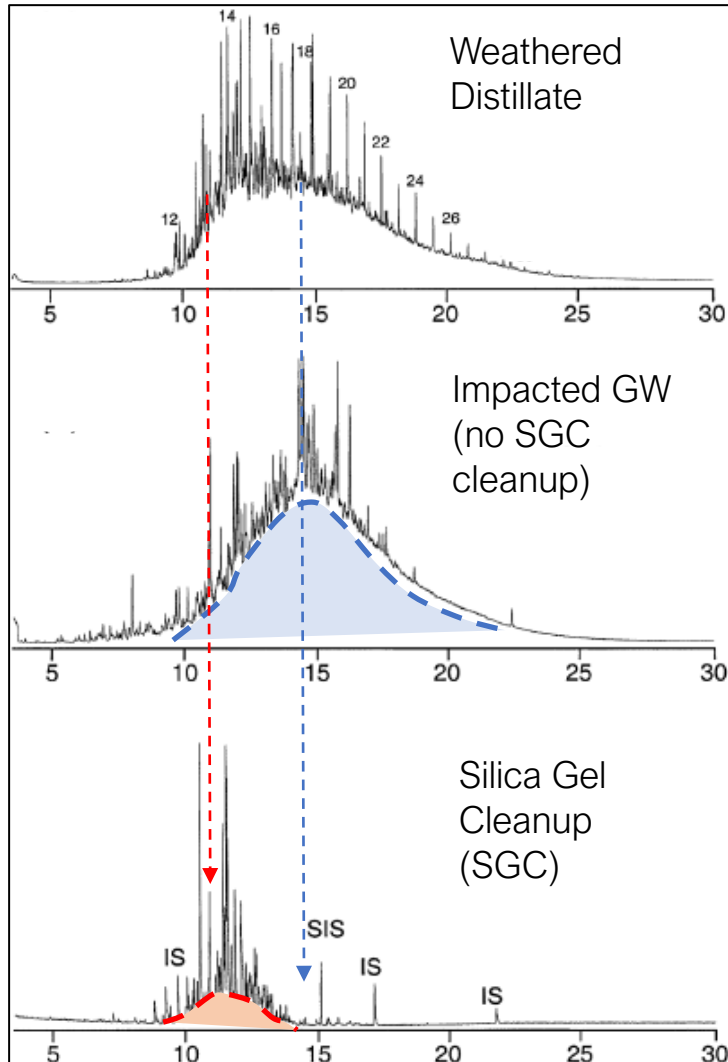


# Purpose of Method



- The purpose of the method is to measure the dissolved fraction of total petroleum hydrocarbons and polar petroleum metabolites in aqueous matrices (C<sub>8</sub> to C<sub>20</sub> carbon range).
- The method utilizes a direct aqueous analysis using SPME technology via GC/FID and GC/MS
- The method can be used in conjunction with standard aqueous TPH analysis using liquid-liquid solvent extraction to better understand aqueous TPH data

# Limitations of Standard TPH Analysis



## Unanswered Questions:

- What is the concentration of the dissolved fraction?
- What is the composition of the dissolved metabolite fraction?
- What is the toxic fraction?

# Method Benefits



- The method can accommodate small sample volumes (~20 – 50 mL)
- The method does not require liquid-liquid solvent extraction using large volumes of organic solvents
- The method can provide a bulk measurement of both dissolved non-polar petroleum hydrocarbons and polar petroleum metabolites
- The method is more sensitive than standard TPH analysis and can be used to evaluate the extent of exposure, and the dissolved carbon range of source materials at GW fuel release sites

# Method Limitations

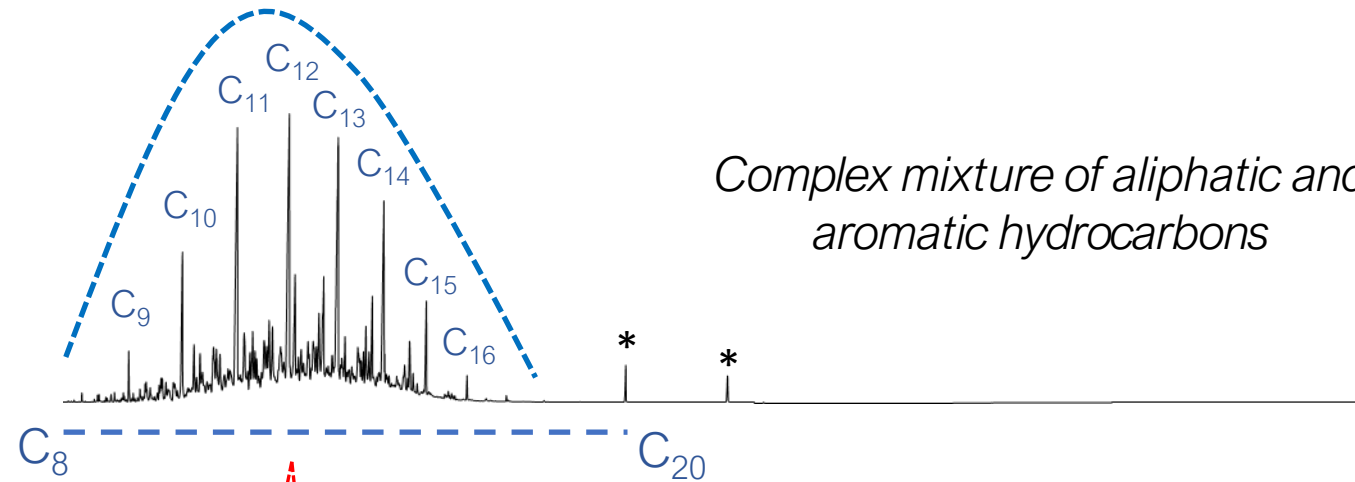


- The method can only be applied to dissolved phase TPH. The method is not suited for aqueous matrices with colloidal LNAPL or sheening
- The method does not provide any mass specific speciation of individual chemicals
- Each sample needs to be run in replicate to ensure data reproducibility. This leads to longer analytical times
- Currently, there are no water quality standards for this type of data, so the SPME method would need to be used as a screening method with other standard methods

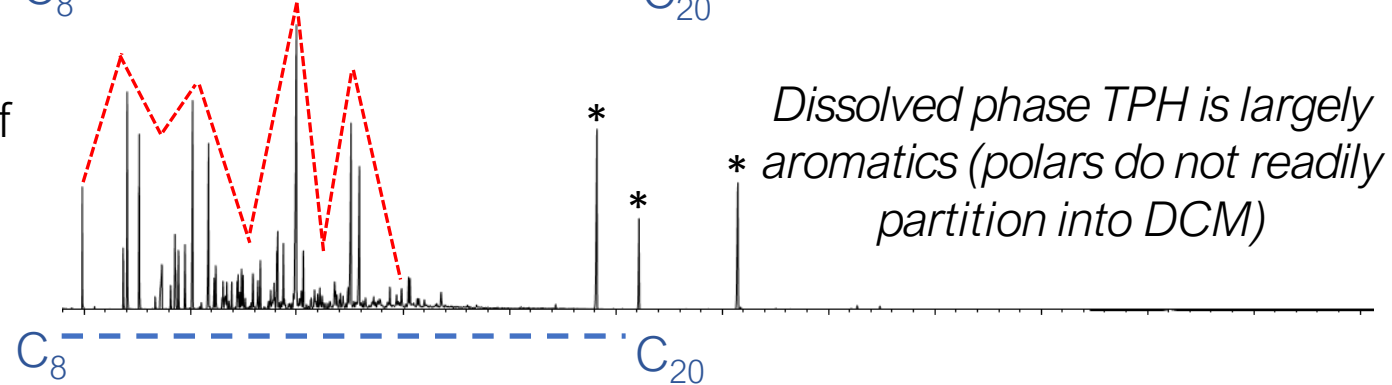
# Ex. Petroleum Release Site



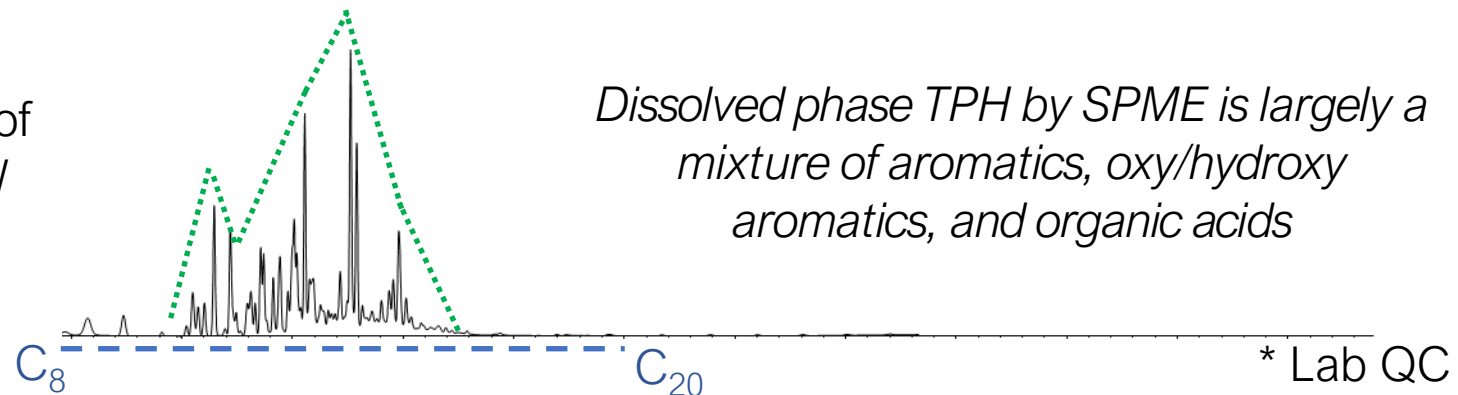
LNAPL Recovered from Site



Dissolved Fraction of TPH Impacted GW Liquid-Liquid TPH



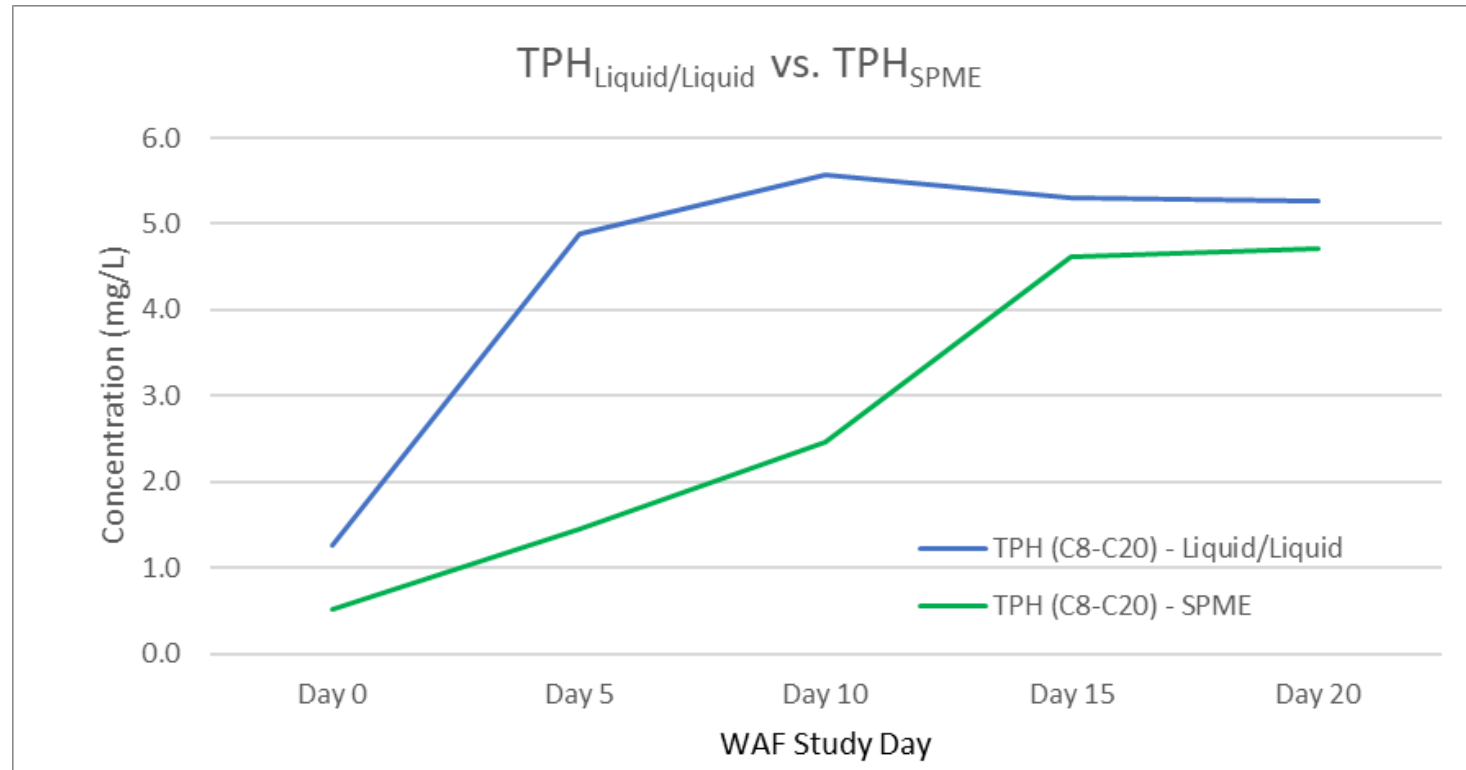
Dissolved Fraction of TPH Impacted GW SPME TPH



\* Lab QC

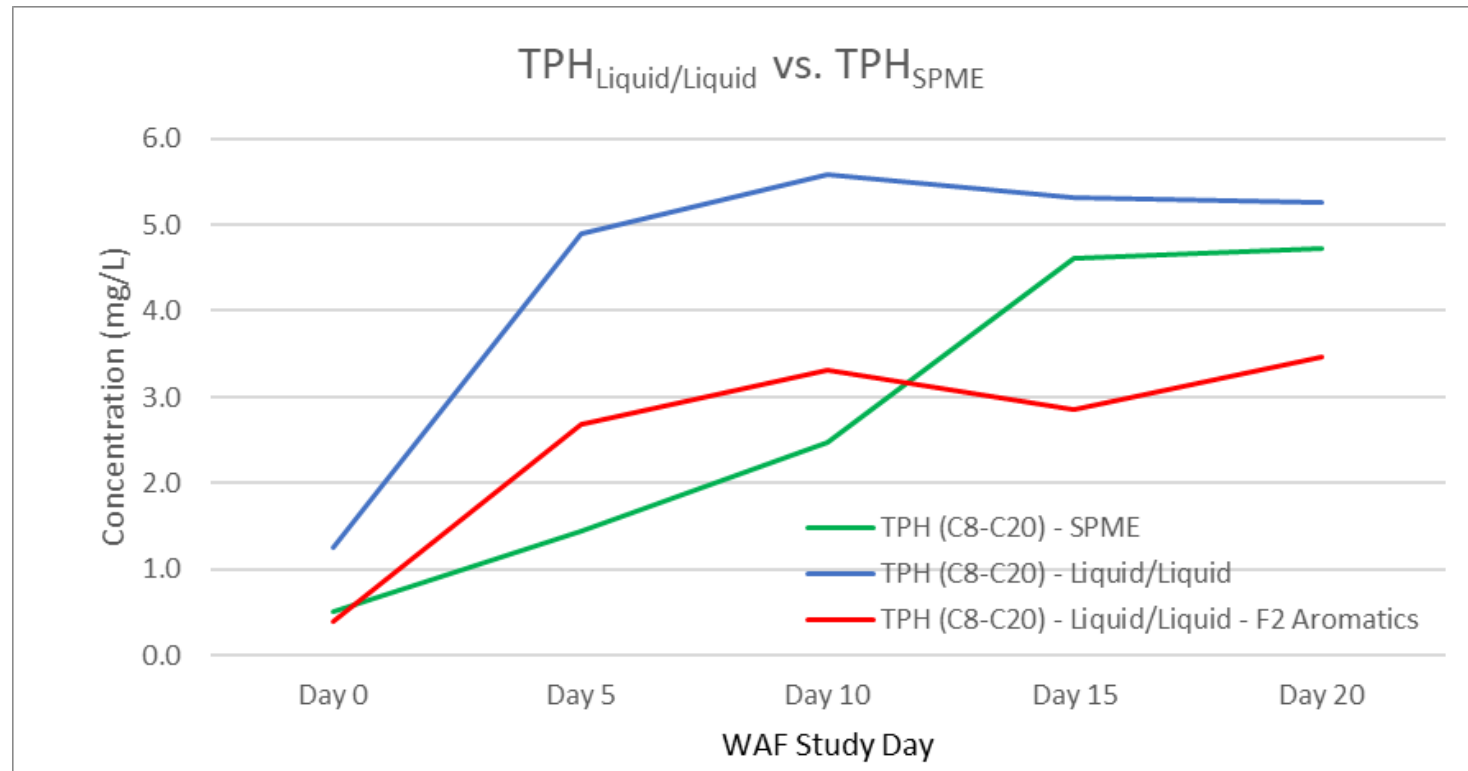


# WAF Samples: TPH<sub>Liquid/Liquid</sub> vs. TPH<sub>SPME</sub>



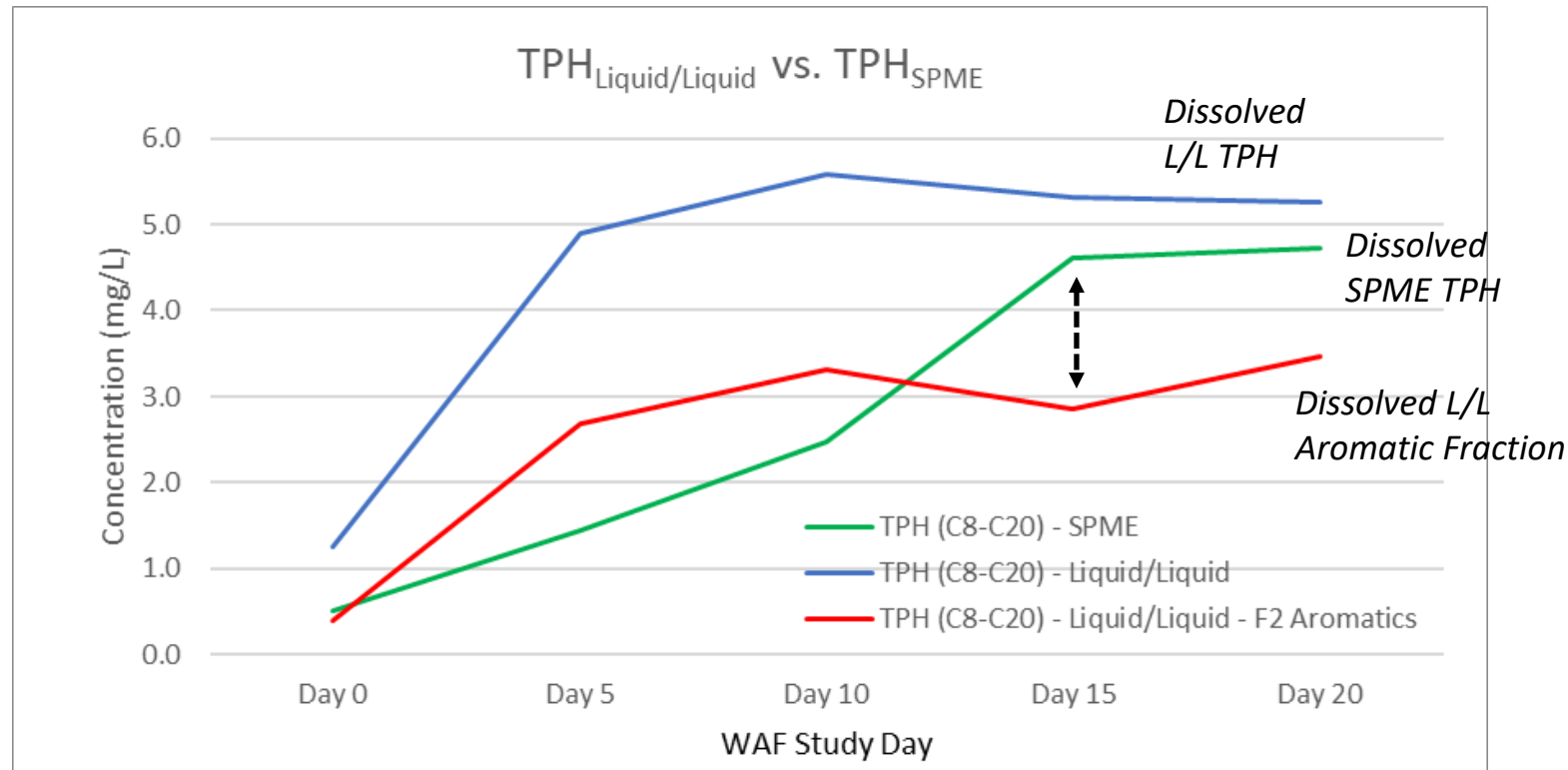
- Synoptic WAF study was conducted to evaluate the two methods
- Results from both methods covary
- Both methods show WAF samples reached a saturation point between Day 10 and 15

# WAF Samples: TPH<sub>Liquid/Liquid</sub> vs. TPH<sub>SPME</sub>



- Aliphatic and Aromatic fractions of standard TPH provide additional data on the composition of petroleum residues
- This data shows that the aromatic fraction makes up a smaller relative part of the total dissolved TPH composition

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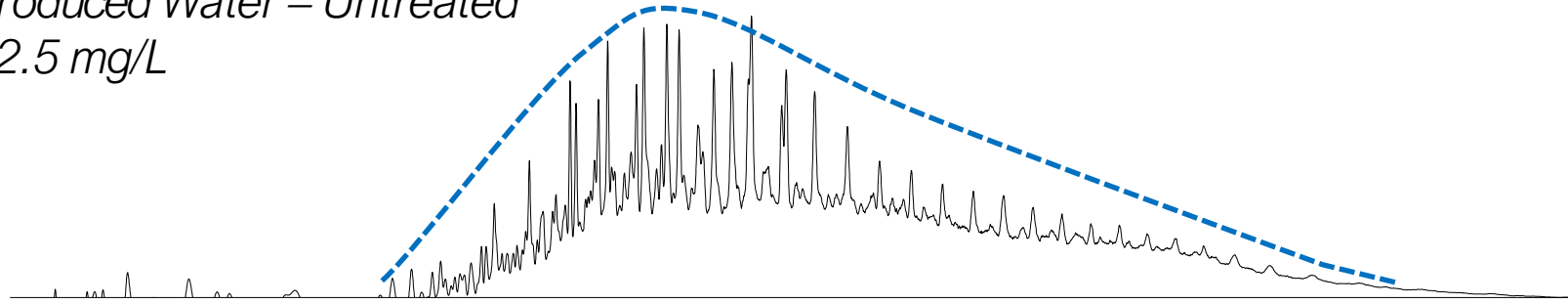


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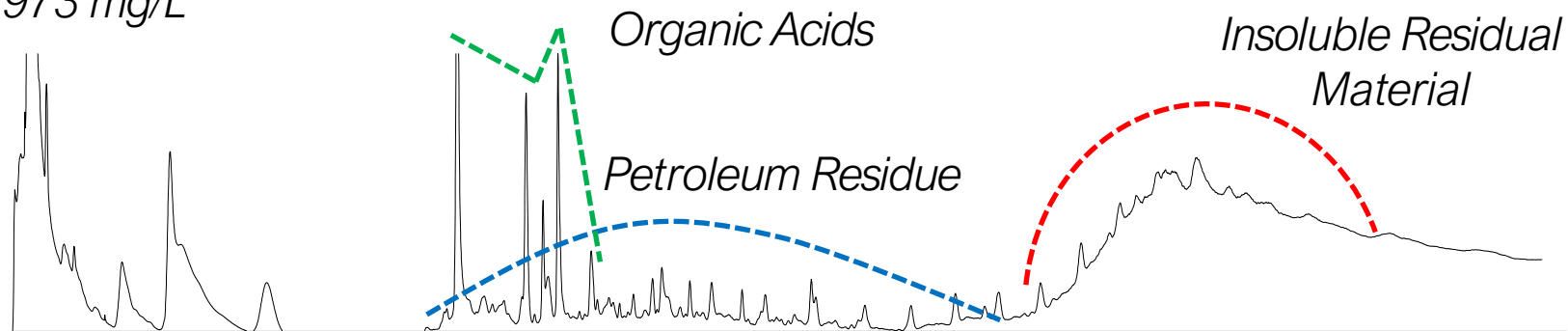
# Produced Water Screening



*Produced Water – Untreated*  
12.5 mg/L



*Produced Water – Treated*  
0.973 mg/L



- The SPME TPH method can be used to screen treated produced waters for the presence of dissolved non-polar and polar petroleum hydrocarbons and metabolites

# Discussion



- The SPME TPH approach is well suited for aqueous samples with dissolved phase petroleum
- If there is colloidal LNAPL or sheening this method will not be effective
- Currently the method is useful as a screening tool and should be used in conjunction with standard aqueous TPH analysis (liquid-liquid)
- Aliphatic and Aromatic fractions of standard TPH provide additional context to the composition of TPH
- GCxGC-FID/ToF SPME method development is in progress to further speciate the dissolved fraction of TPH by increasing orders of polarity

# Acknowledgements



The laboratory analysis was conducted at *Alpha Analytical, Inc.* in Mansfield Massachusetts. Alpha is NewFields partner organization in Forensic Chemistry and method development



# Questions?

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