TNI Environmental Measurement Symposium

St. Louis, Missouri

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Advanced Forensic Fuel Fingerprinting Using Comprehensive Two-Dimensional Gas Chromatography

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Introduction

- Limitations of Conventional GC-FID Petroleum Fingerprinting
- GC x GC Separations: Molecular Weight and Polarity or Unsaturation
- GC x GC Petroleum Fingerprinting
  - Resolving diagnostic compositional features
  - Measuring more highly resolved petroleum fractions
- GC x GC Petroleum Reference Materials Fingerprints
  - Jet Fuels, Mineral Oil, and Diesel-Biodiesel

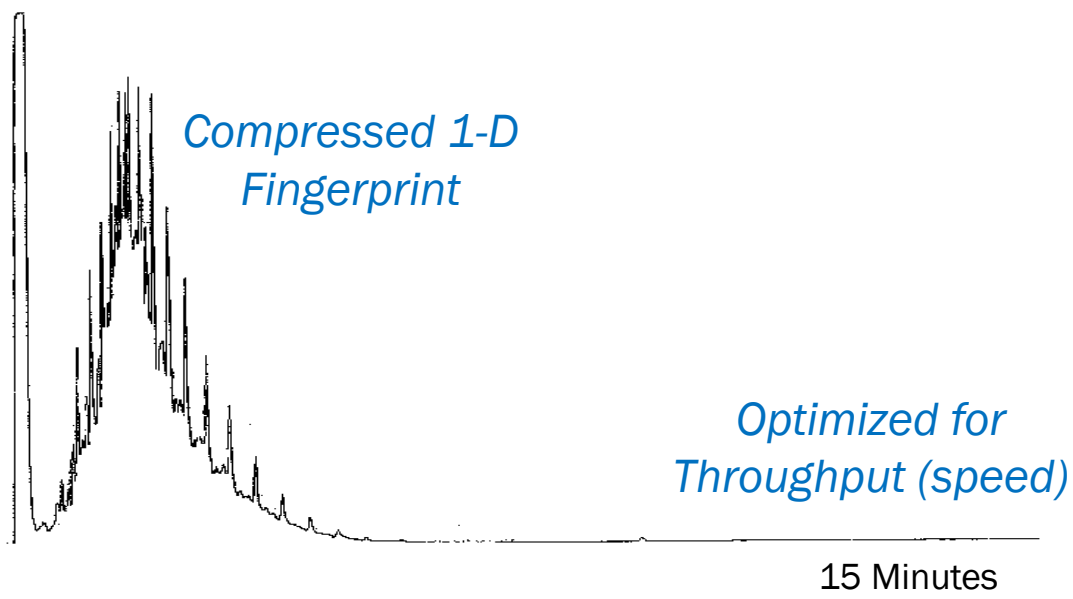
GC x GC Petroleum Measurements in Marine Sediment

- Separating Petroleum from Naturally Occurring Organic Matter

Conventional Hydrocarbon Fingerprinting Methods

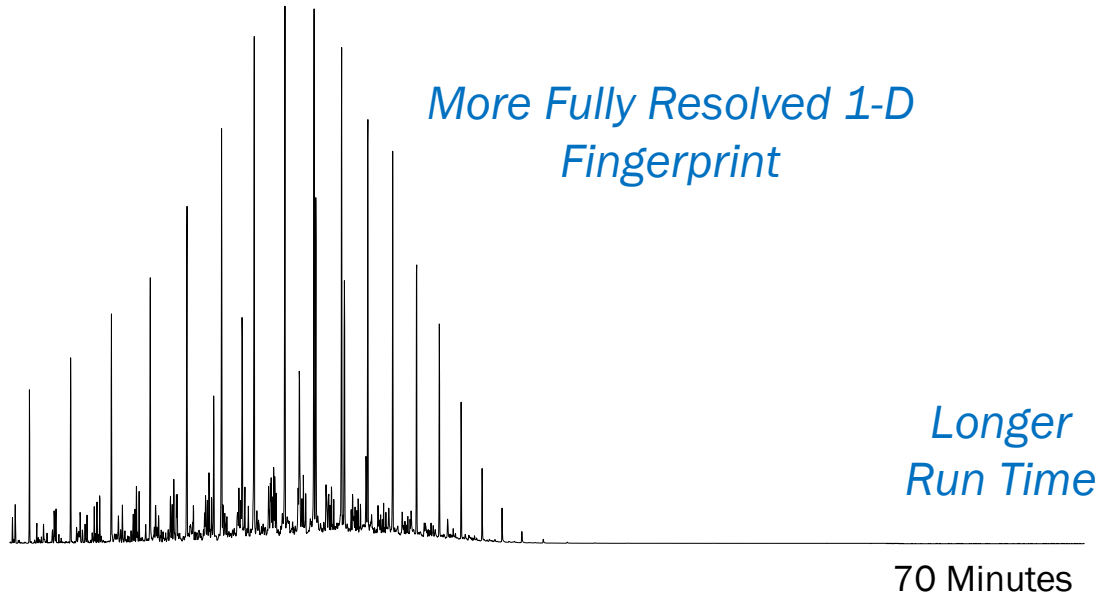
Diesel Fuel Fingerprints by 1-Dimensional GC/FID (EPA Method 8015)

Production Lab



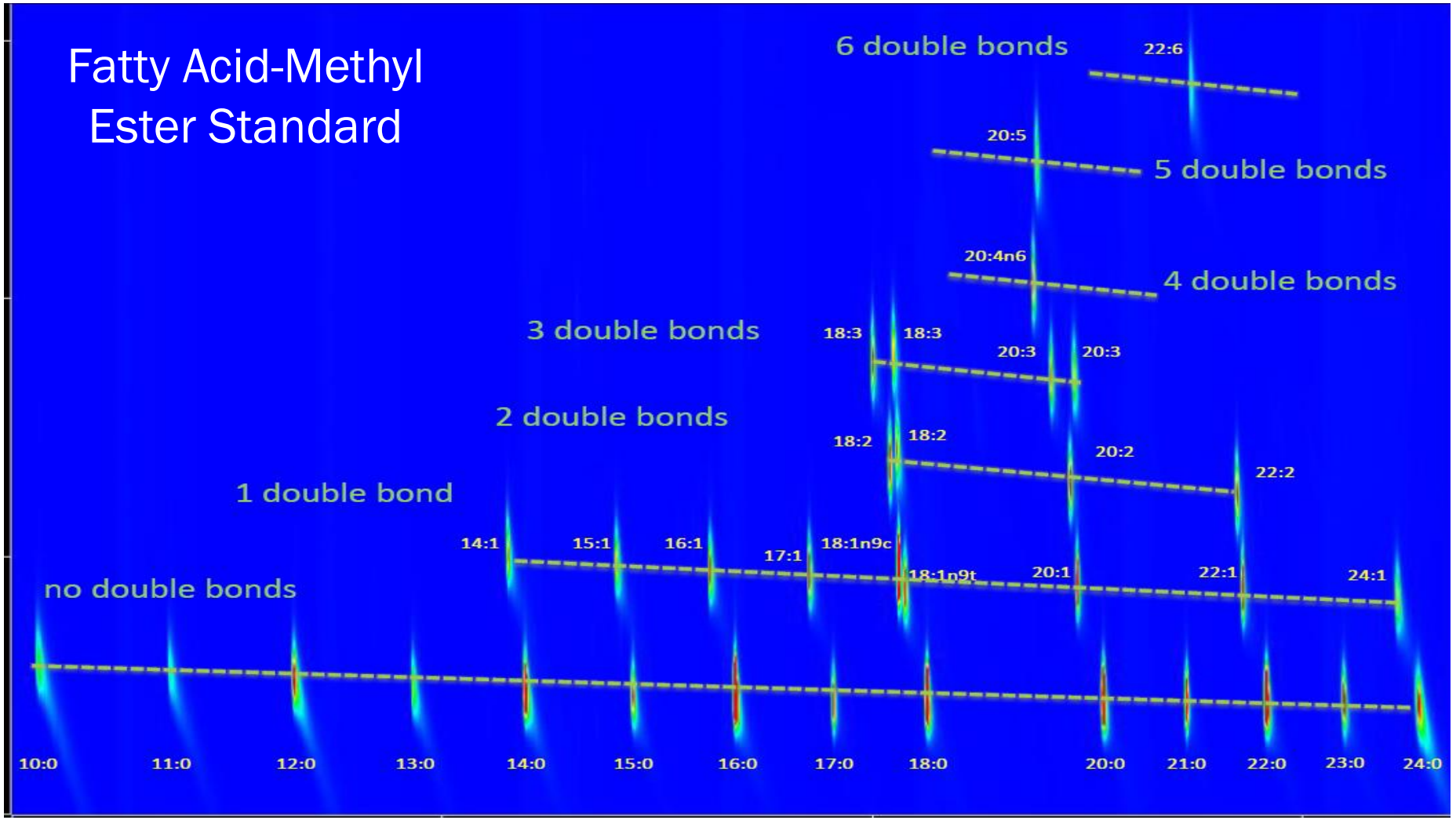
Low Chromatographic Resolution

Conventional Forensic Lab



No Separation of non-polar and polar chemicals

GC x GC Separations: Molecular Weight and Polarity

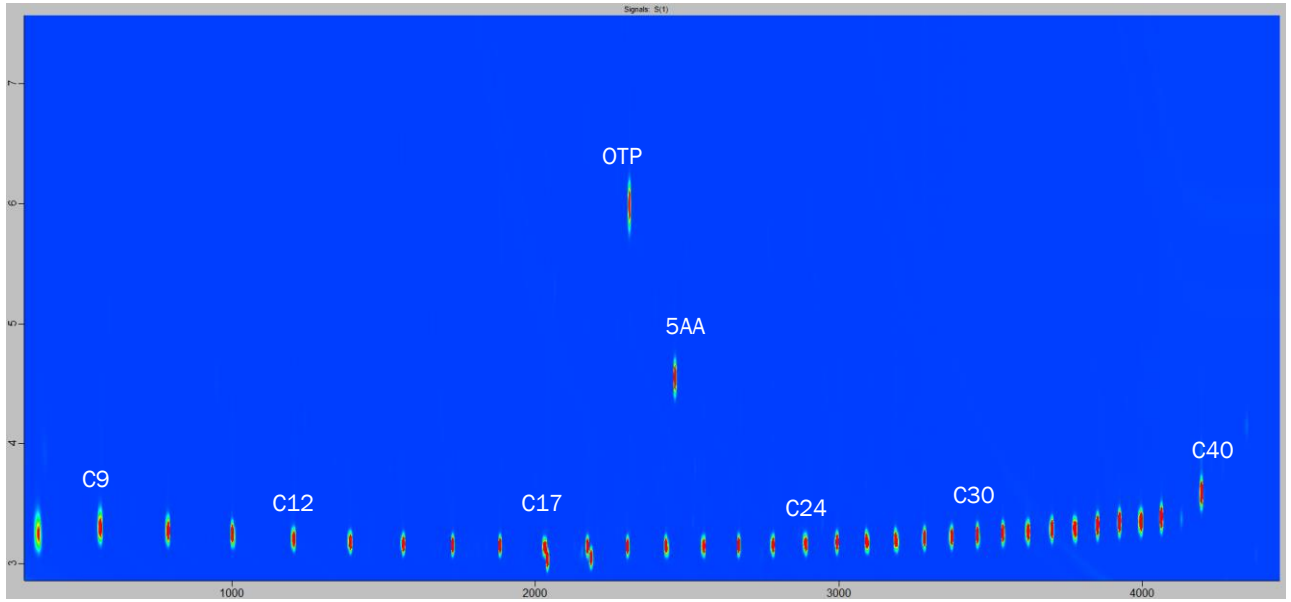


Increasing Polarity - Unsaturation

Increasing Molecular Weight

GC x GC Saturated Hydrocarbon Calibration Curve

Name	Correlation Coefficients	Name	Correlation Coefficients
n-Octane (C8)	0.99454	n-Tricosane (C23)	0.99967
n-Nonane (C9)	0.99994	n-Tetracosane (C24-d50)	0.99964
n-Decane (C10)	0.99996	n-Tetracosane (C24)	0.99964
n-Undecane (C11)	0.99996	n-Hexacosane (C25)	0.99989
n-Dodecane (C12)	0.99999	n-Hexacosane (C26)	0.99992
n-Tridecane (C13)	0.99999	n-Heptacosane (C27)	0.99987
n-Tetradecane (C14)	0.99995	n-Octacosane (C28)	0.99987
n-Pentadecane (C15)	0.99995	n-Nonacosane (C29)	0.99965
n-Hexadecane (C16)	0.99989	n-Triacontane (C30)	0.99493
n-Heptadecane (C17)	0.99981	n-Hentriacontane (C31)	0.99615
Pristane	0.99999	n-Dotriacontane (C32)	0.99387
n-Octadecane (C18)	0.9998	n-Tritriacontane (C33)	0.99518
Phytane	0.99997	n-Tetratriacontane (C34)	0.99903
n-Nonadecane (C19)	0.99994	n-Pentatriacontane (C35)	0.99267
OTP	0.99995	n-Hexatriacontane (C36)	0.99896
n-Eicosane (C20)	0.99974	n-Heptatriacontane (C37)	0.99598
n-Heneicosane (C21)	0.99971	n-Octatriacontane (C38)	0.99559
n-Docosane (C22)	0.99998	n-Tetracontane (C40)	0.99285

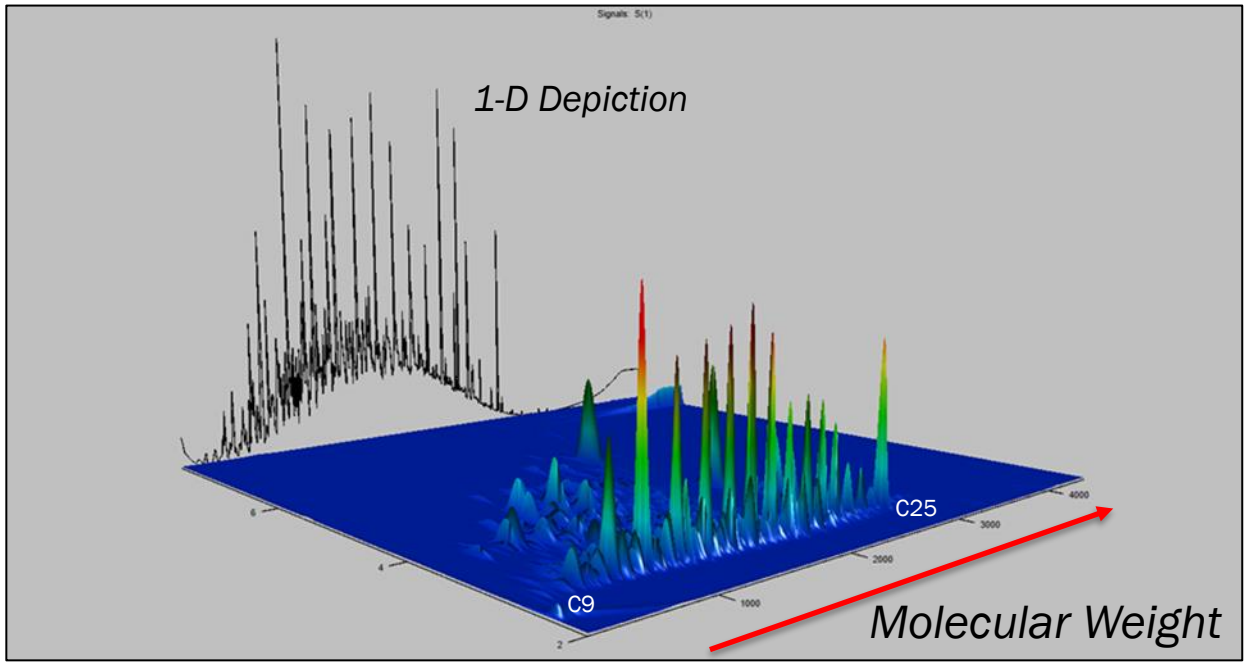


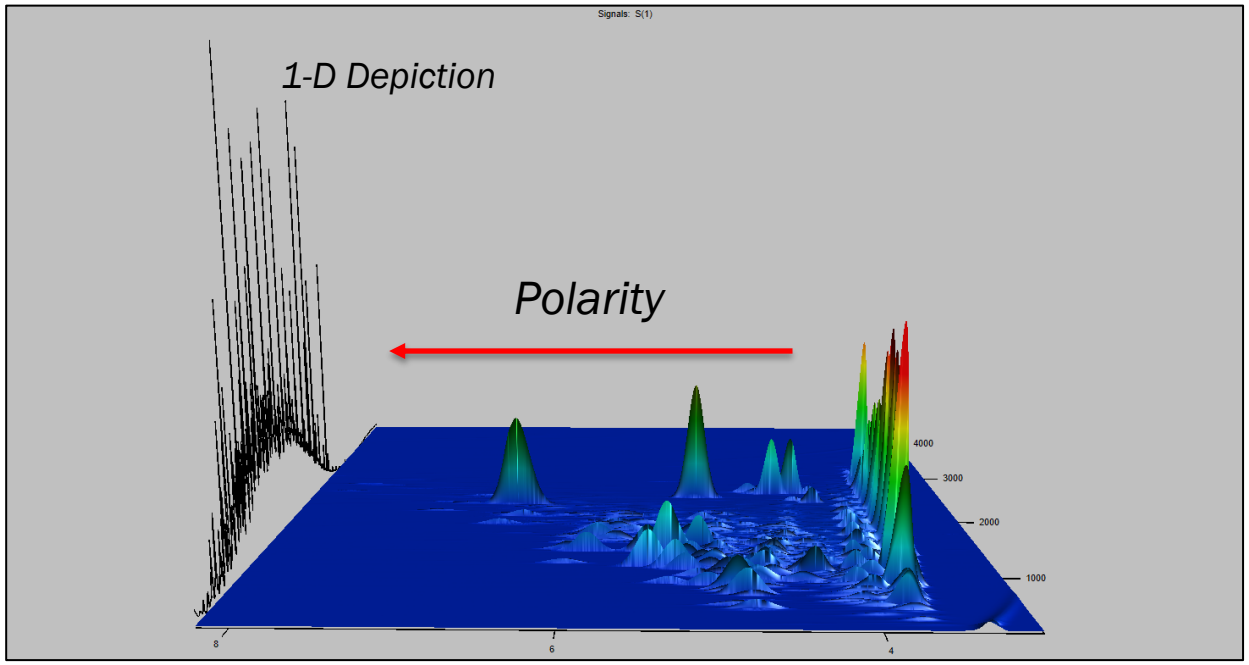
5-Level Saturated Hydrocarbon Calibration Curve: C_8-C_{40}

Average Correlation Coefficient: 0.9985

Reporting Limit: 50 µg/kg

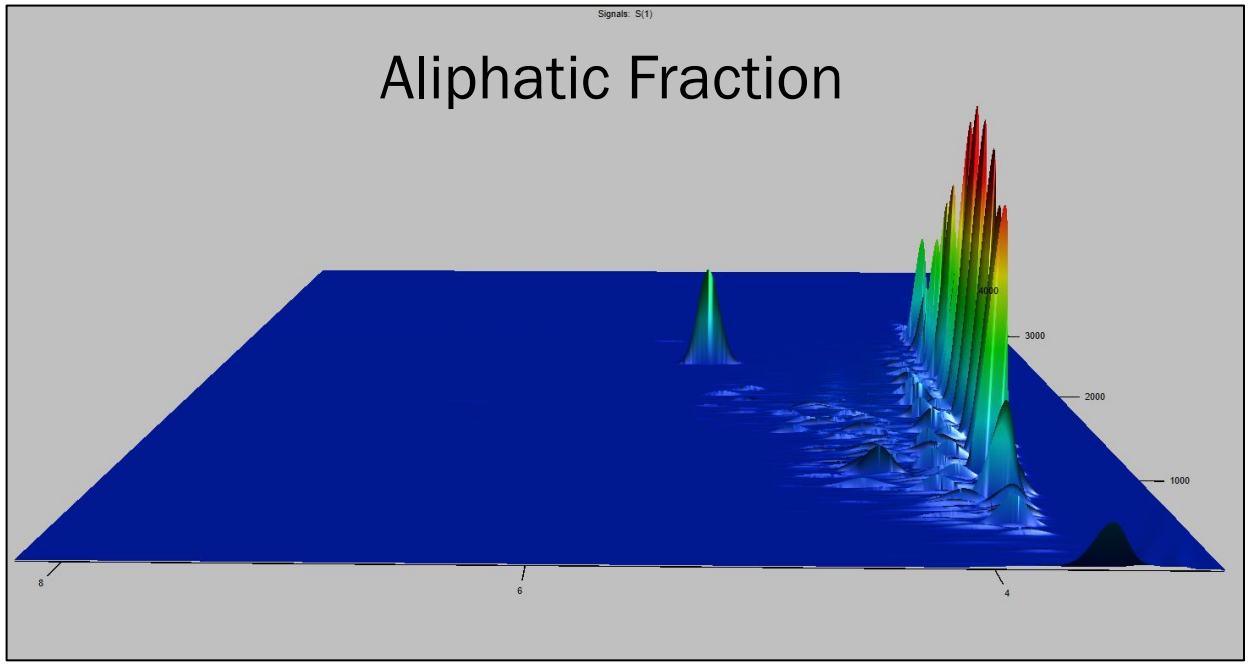
GC x GC Diesel Fingerprint

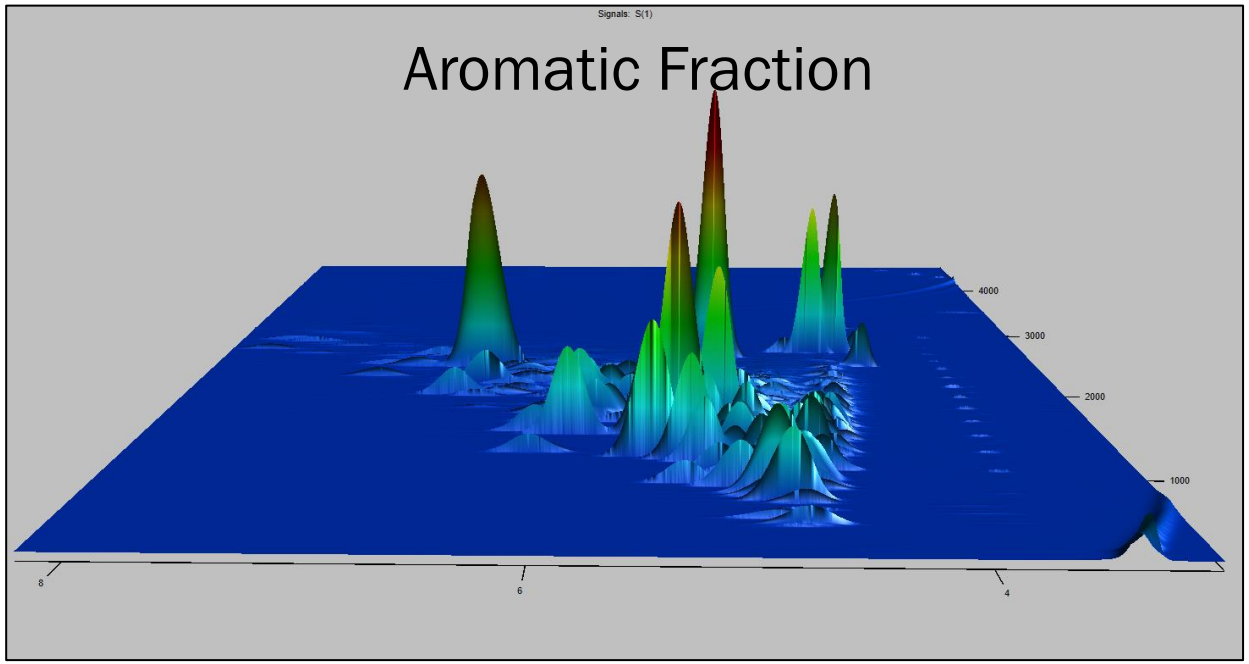




GC x GC separates complex mixtures of petroleum hydrocarbons by molecular weight, and polarity and allows for unique compositional observations and measurements to be made

Diesel Fingerprint: Aliphatic and Aromatic Fractions

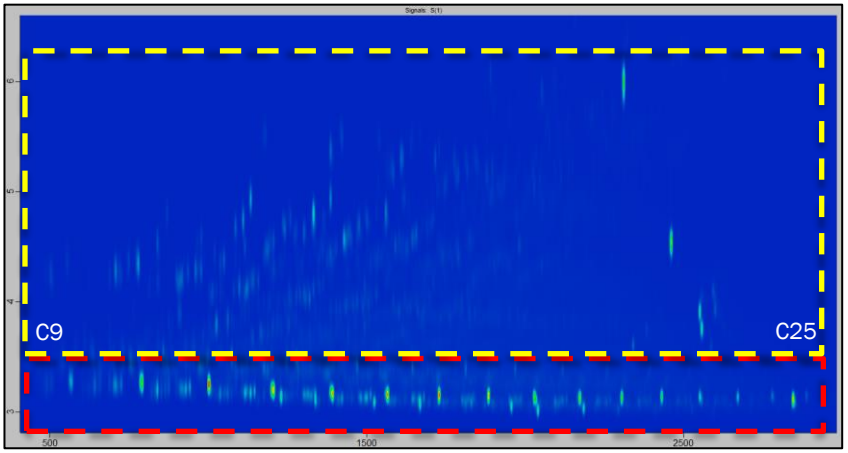




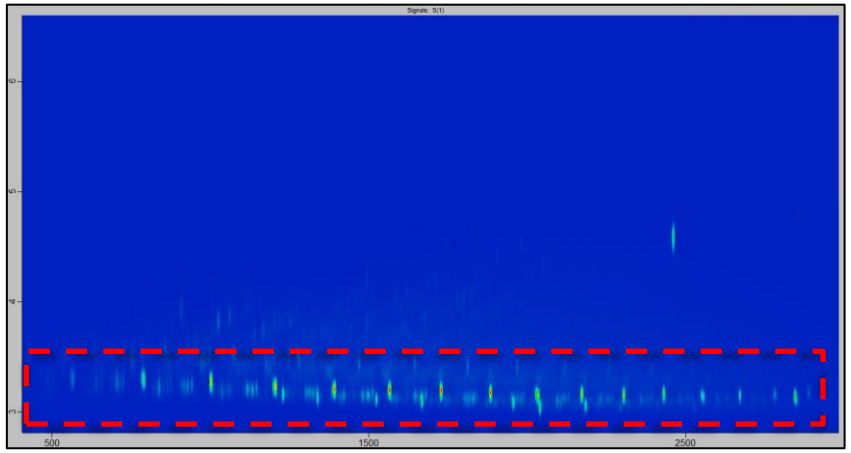
GC x GC allows for defined aliphatic and aromatic carbon ranges to be measured without silica gel fractionation

Diesel Aliphatic and Aromatic Range Measurements

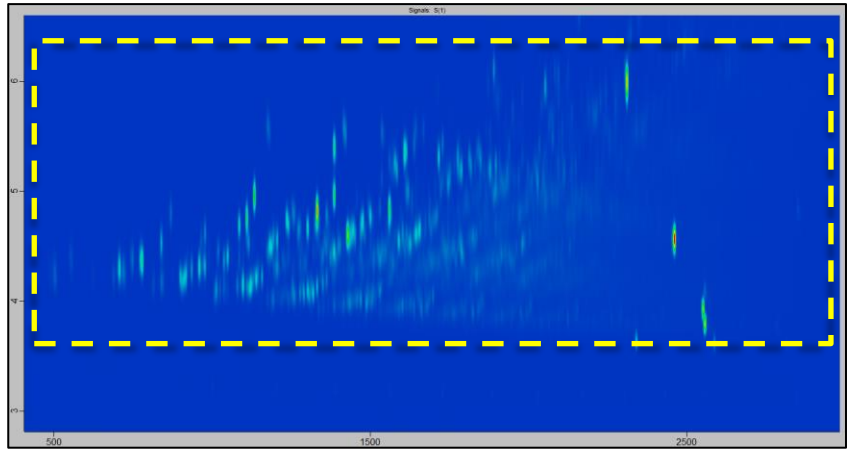
Combined Aliphatic/Aromatic



Aliphatic Fraction



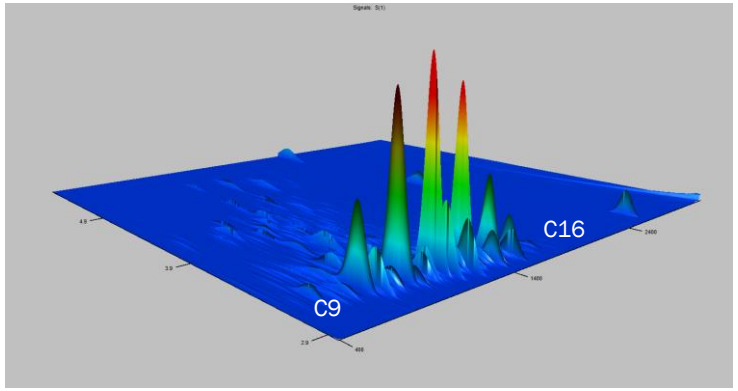
Aromatic Fraction

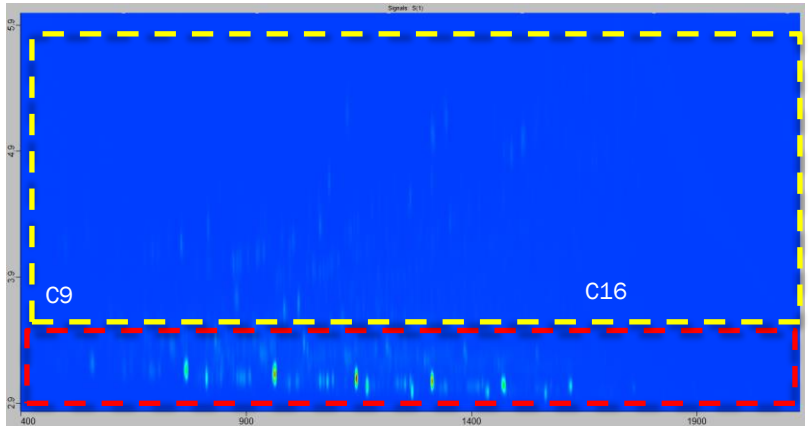


GC x GC allows for defined aliphatic and aromatic carbon ranges to be measured without silica gel fractionation

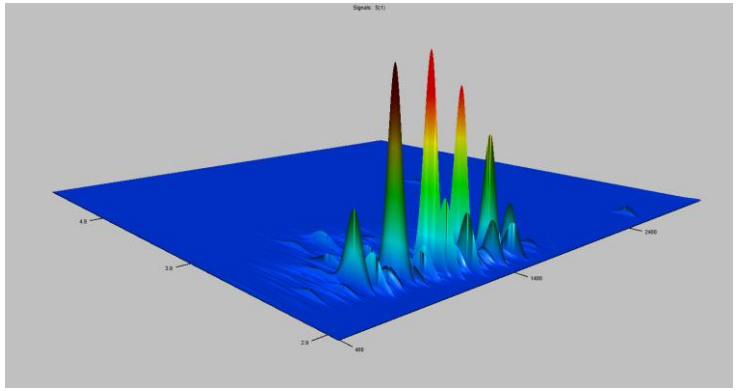
GC x GC Jet Fuel Fingerprints

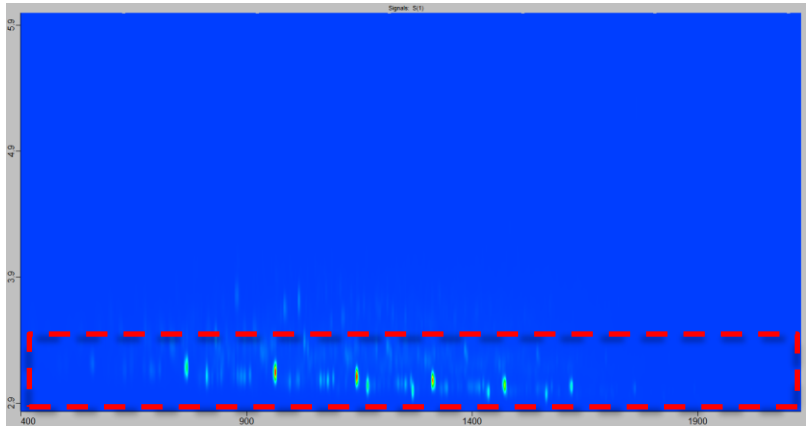
Combined Aliphatic/Aromatic



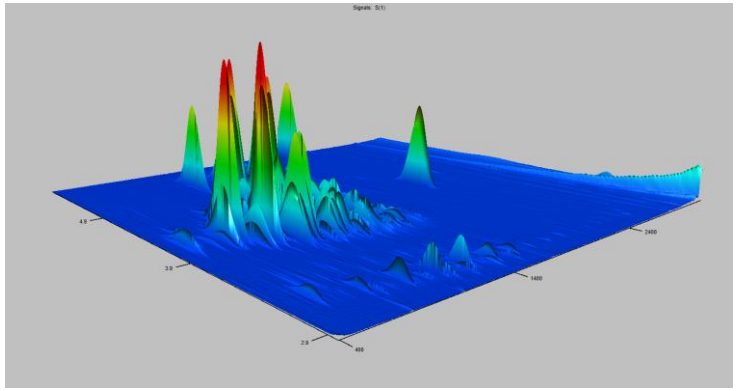


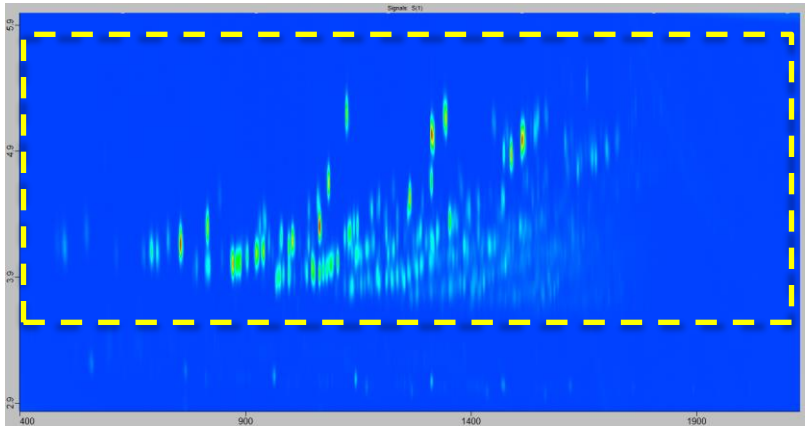
Aliphatic Fraction





Aromatic Fraction

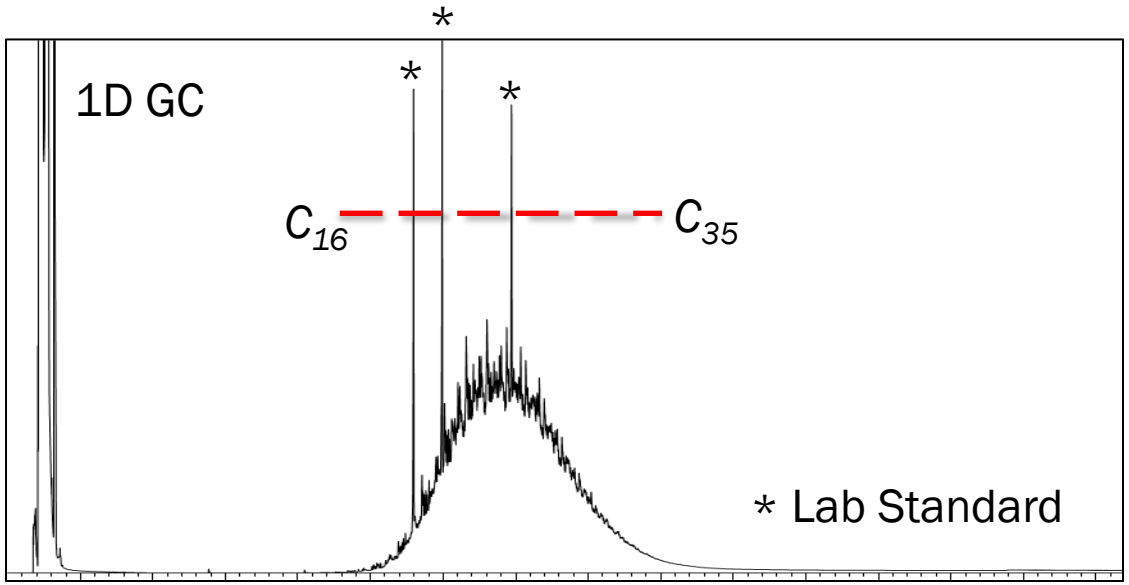


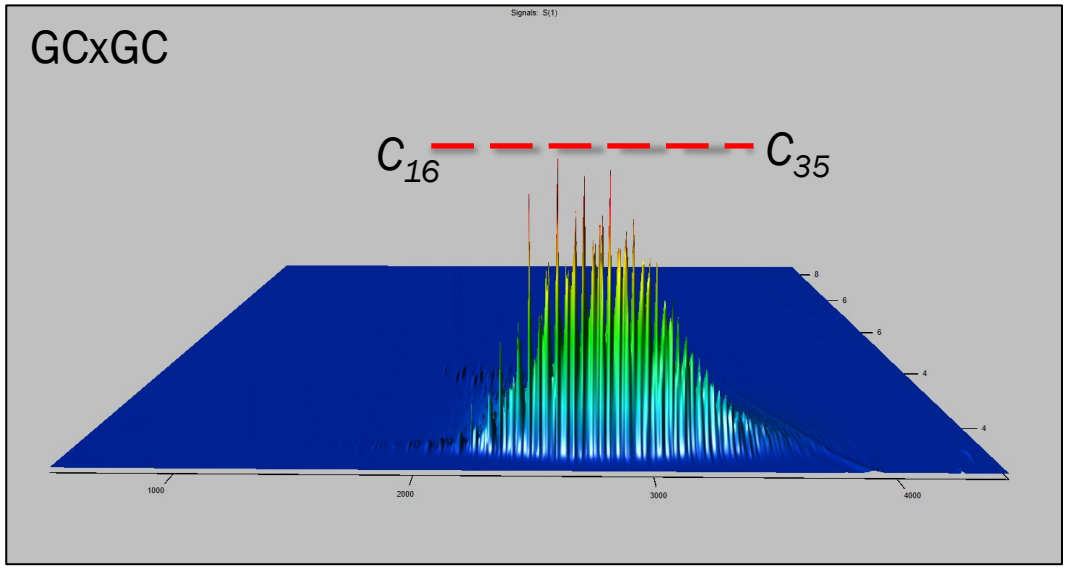


GC x GC separations provide diagnostic compositional information and provides carbon range measurements potentially useful in risk assessment

Mineral Oil: GC x GC vs. 1-D GC Fingerprint

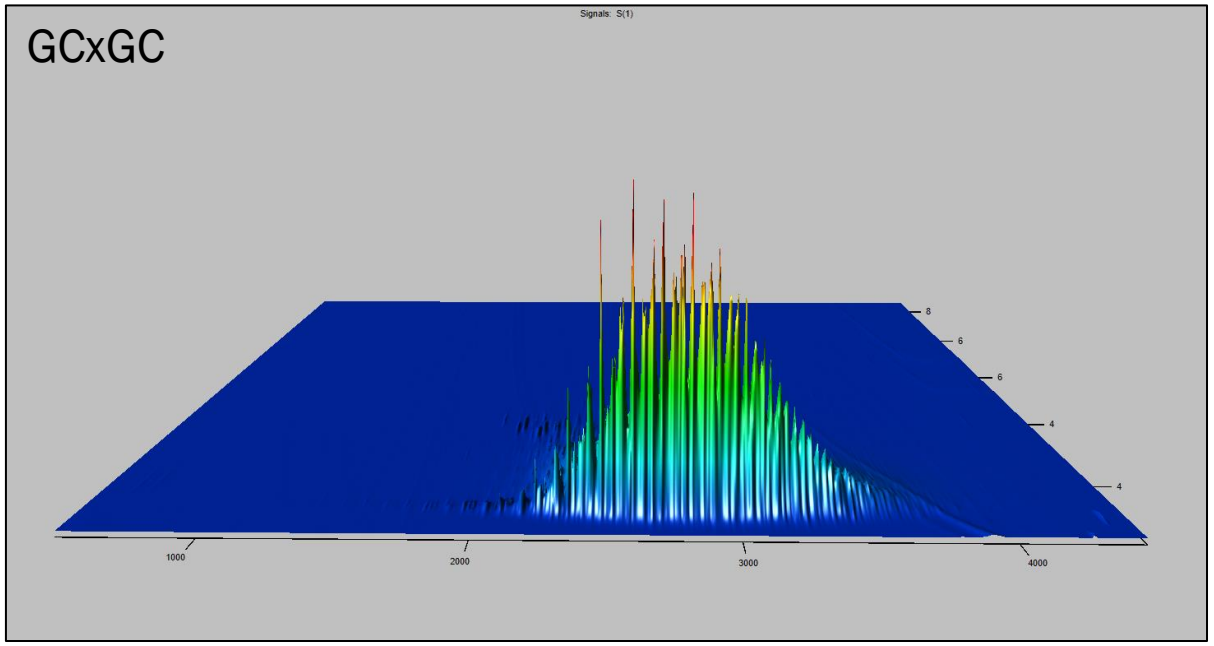
Chromatograms of the same Mineral Oil

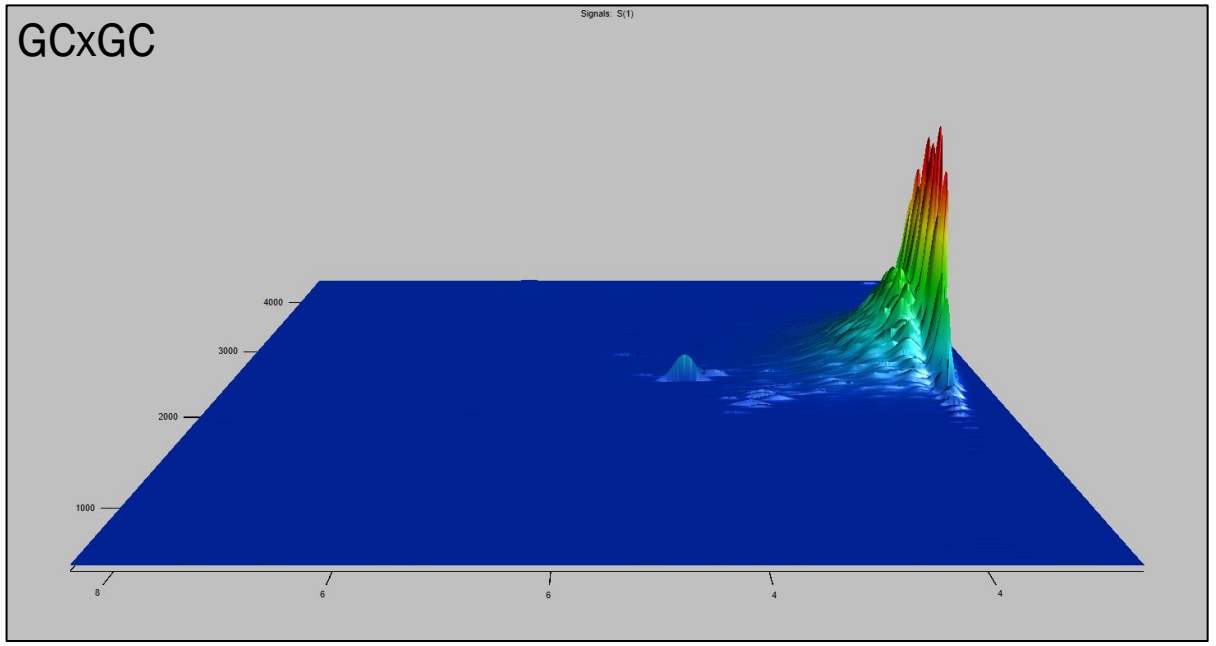




GC x GC and 1-D GC Fingerprints both provide molecular weight separations that allow for the carbon and boiling ranges of petroleum products to be determined

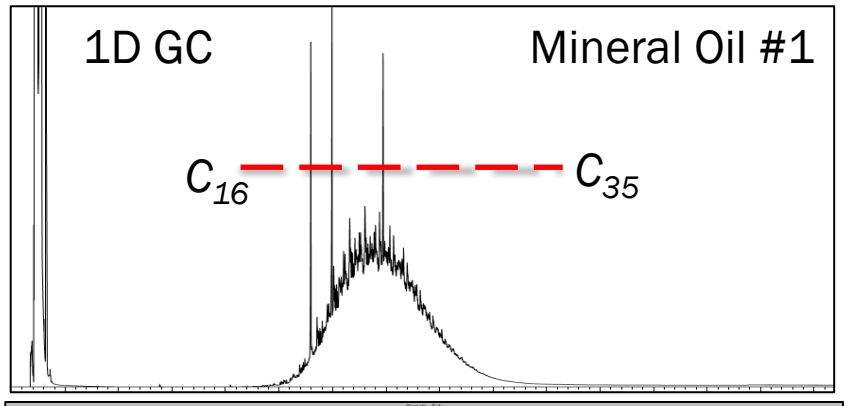
Mineral Oil: Alkane vs. Cyclic Composition

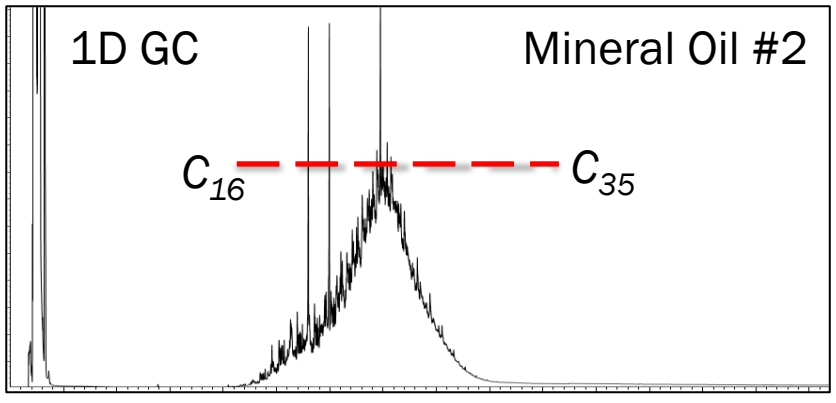


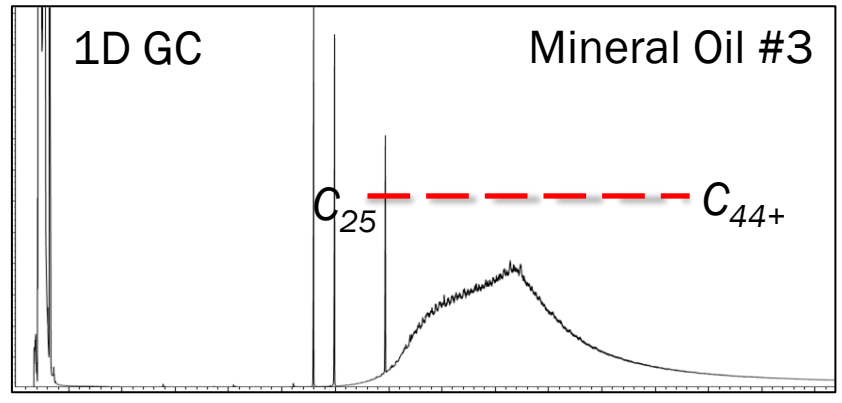


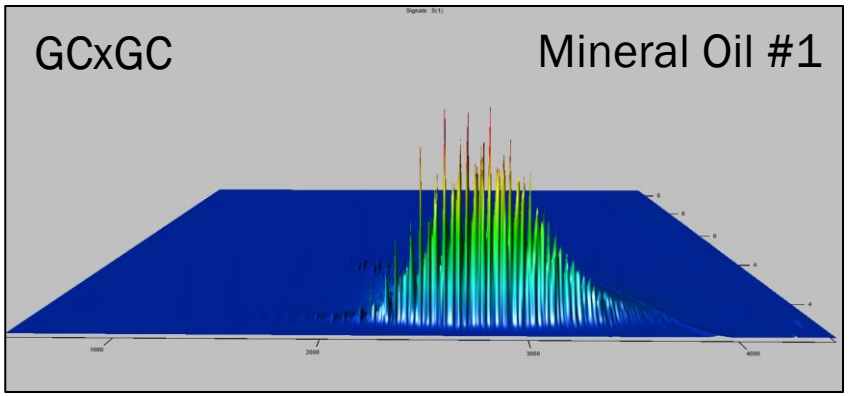
GC x GC separates cyclic (naphthenes) and straight chain (n-alkanes) aliphatic hydrocarbons and allows for a compositional assessment not observable by 1-D GC.

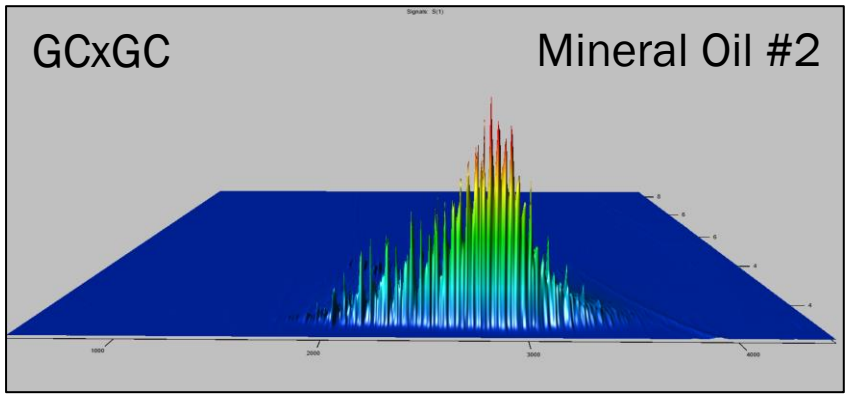
Differentiating Source: Carbon Range and Composition

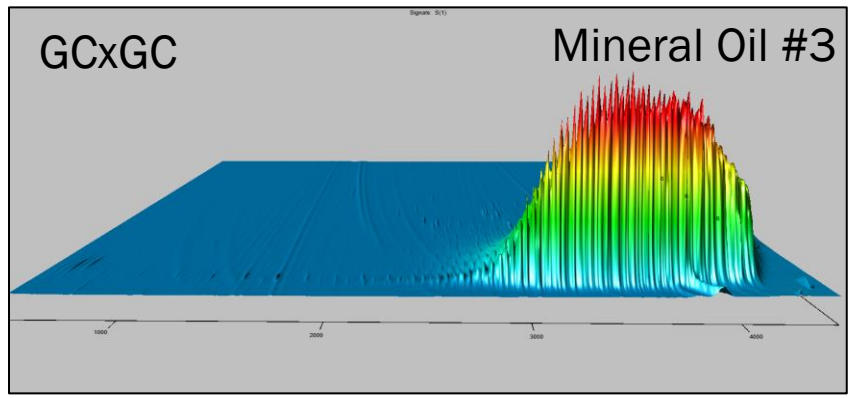


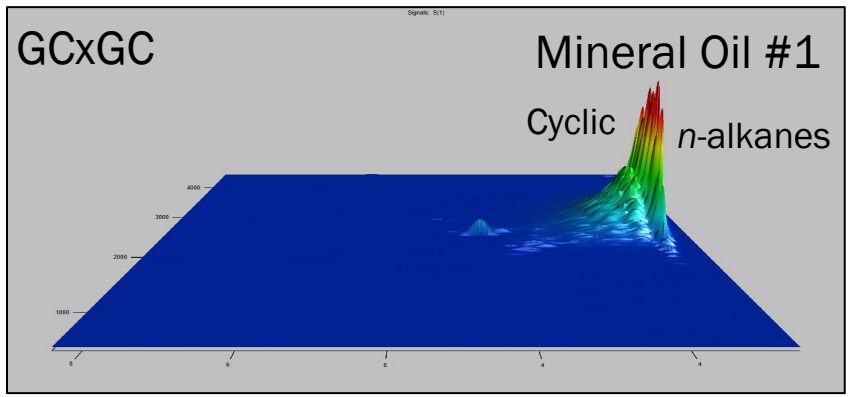


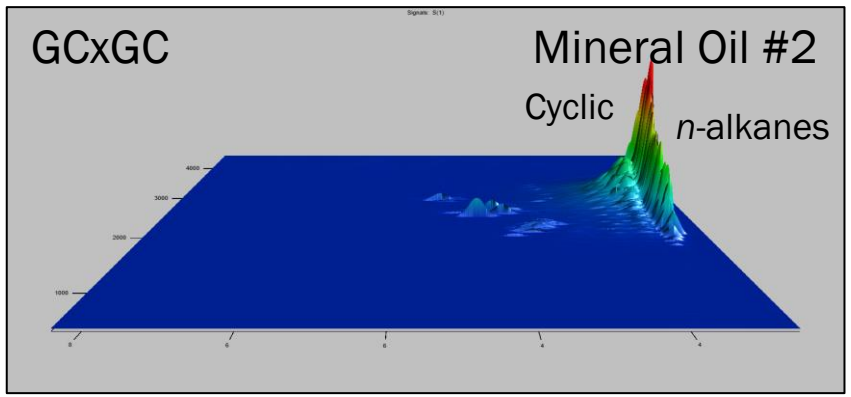


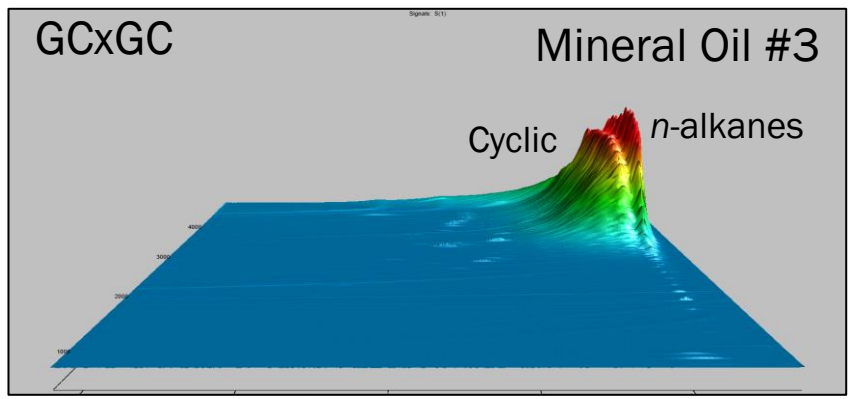




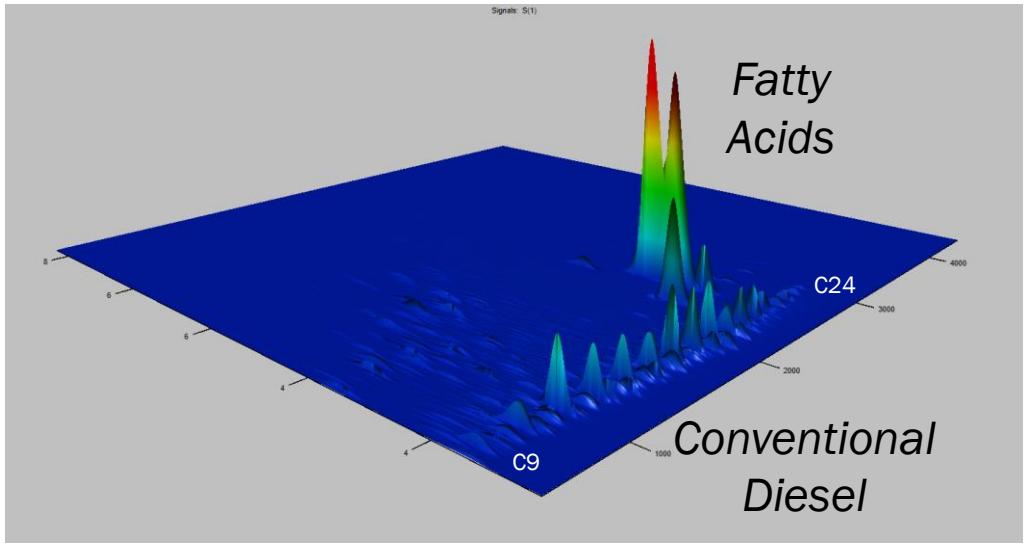


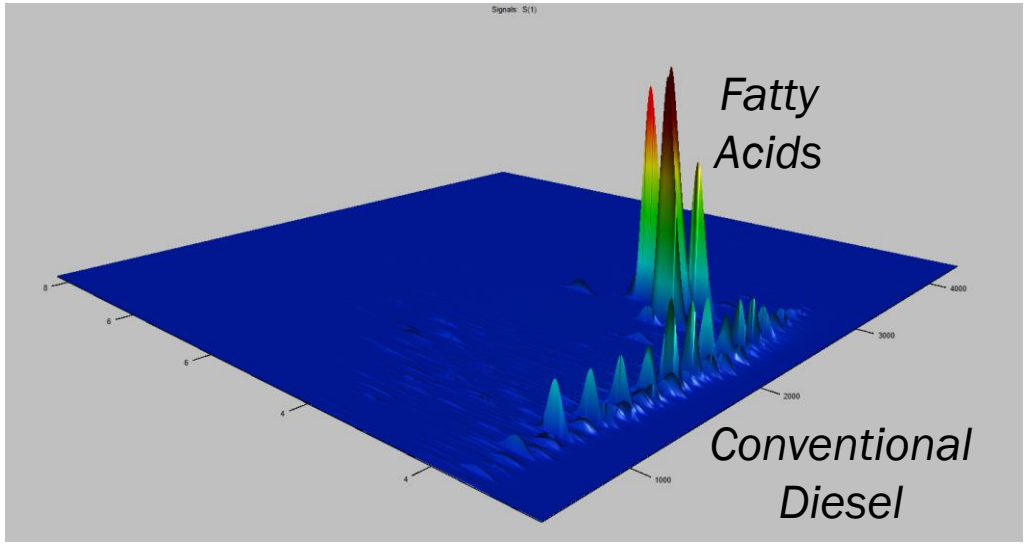


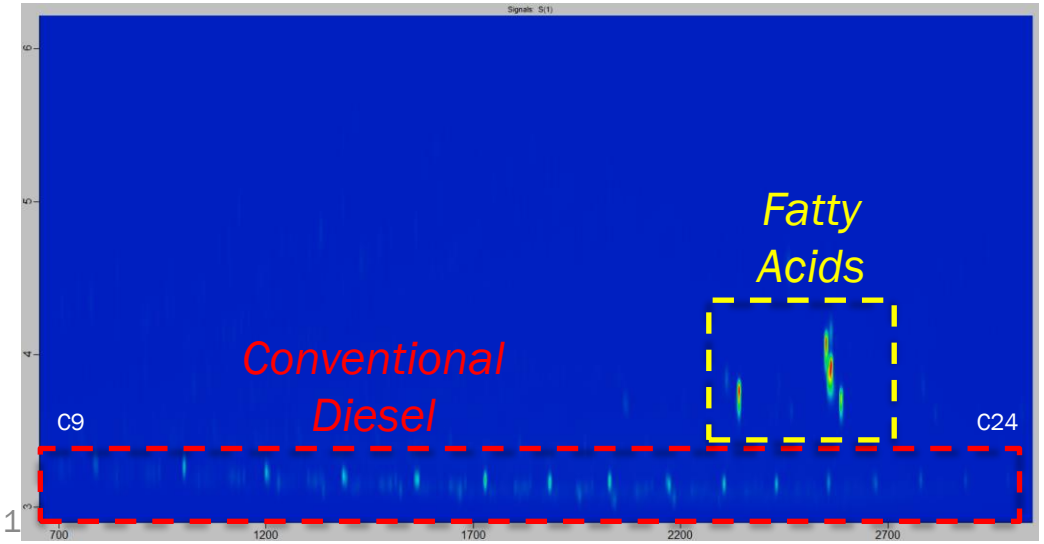


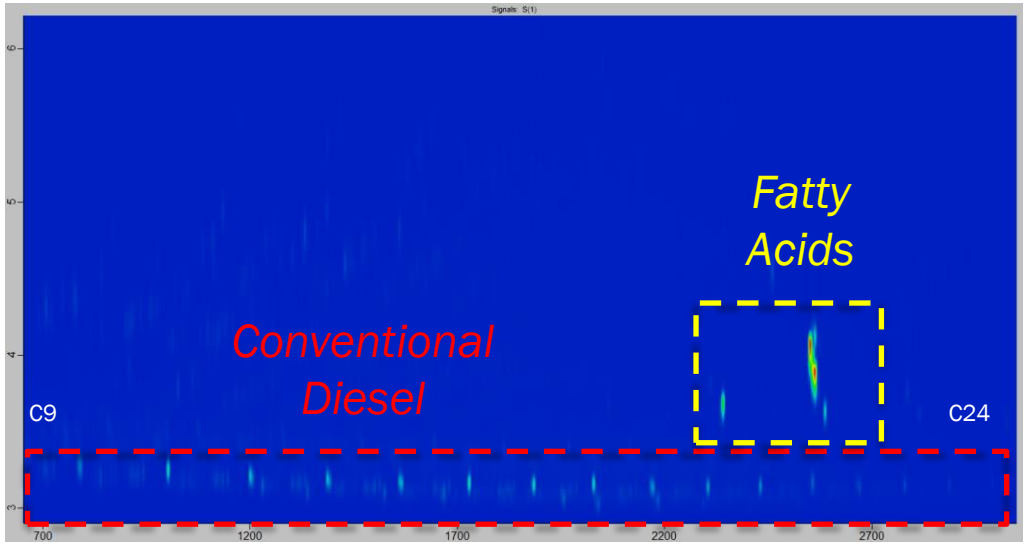


GC x GC Biodiesel Fingerprints and Separations

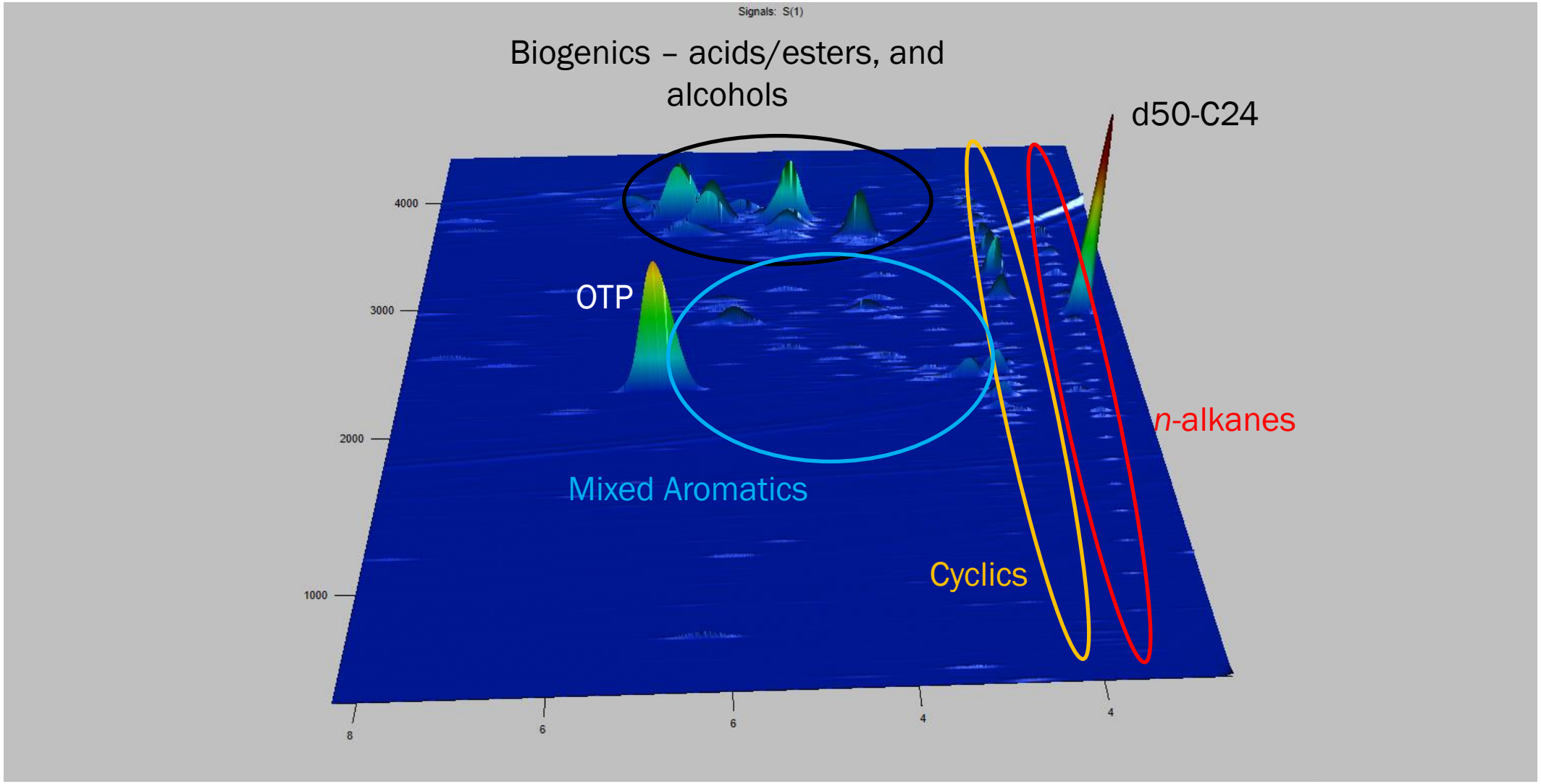








GC x GC Marine Sediments: Naturally Organic Matter



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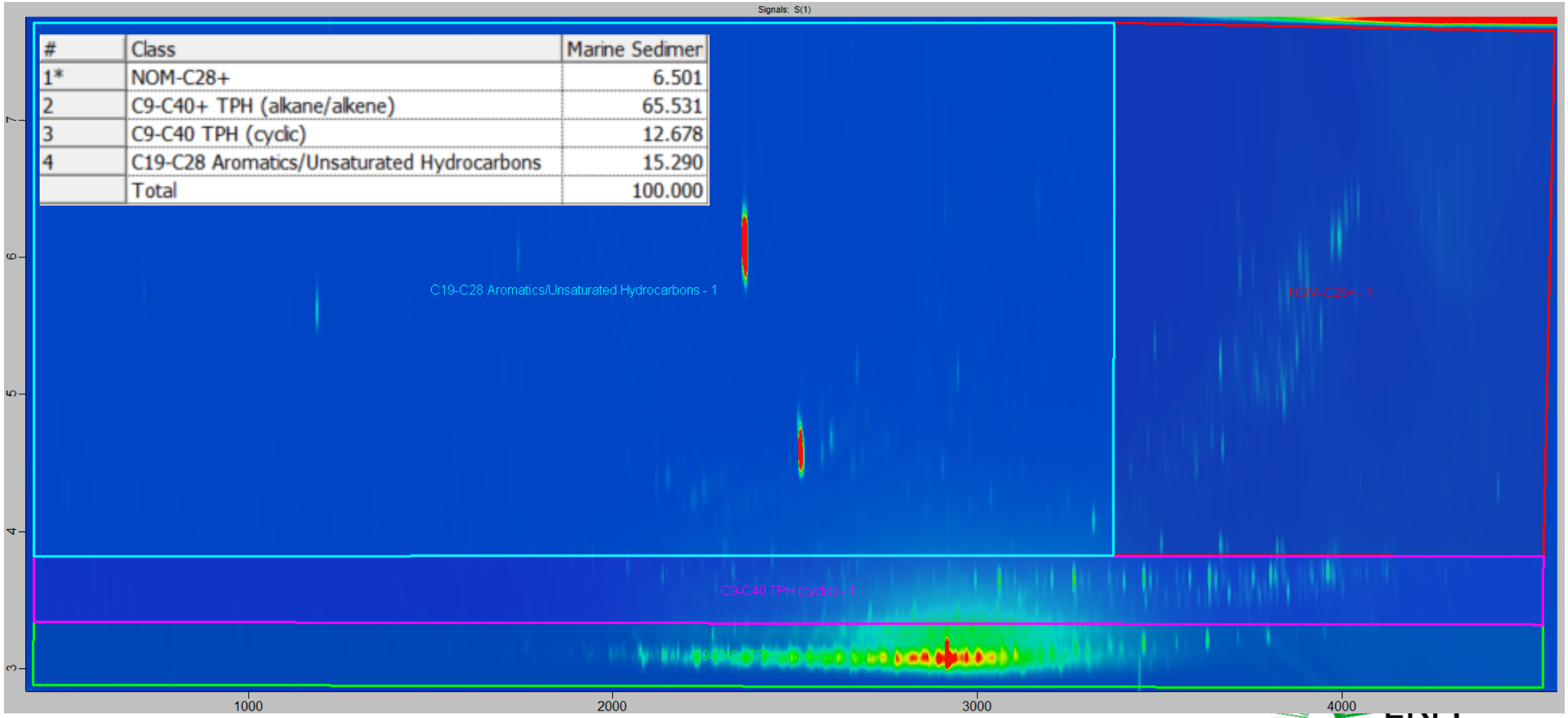

#	Class	Marine Sedimer
1*	NOM-C28+	6.501
2	C9-C40+ TPH (alkane/alkene)	65.531
3	C9-C40 TPH (cyclic)	12.678
4	C19-C28 Aromatics/Unsaturated Hydrocarbons	15.290
	Total	100.000

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Questions?

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