Oil Spill Source Identification with Advanced and Tiered Analytical Tools

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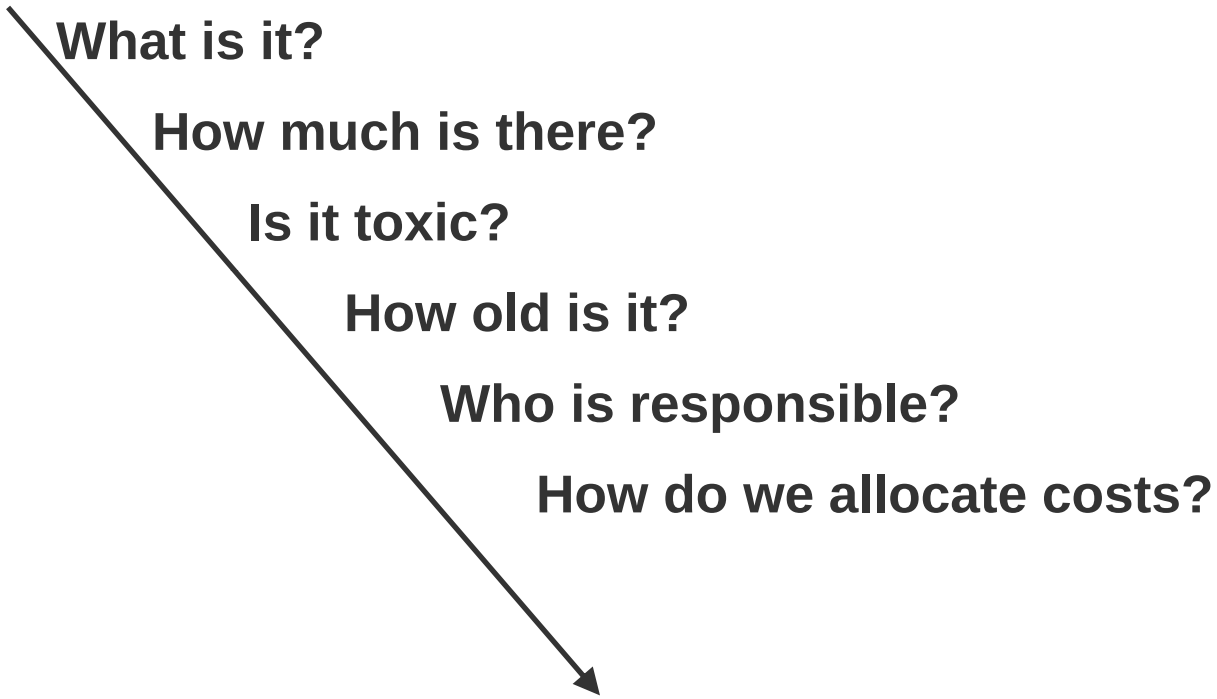
Goal of Analysis – Data Quality Objective



Increasing cost, time, interpretive skill, fuzziness, and …

Source Identification

- **You would like :**
  - Clarification ownership
- **You usually get:**
  - Most Likely
  - Multiple contributions
  - Relative description – hypothesis
  - Inconclusive or paradoxical results
- **You need to use:**
  - Multiple lines of evidence

Petroleum Product – Specifications

- Specifications are designed to meet customer's performance requirements
- Customer specifications include:
  - Engine performance
  - Environmental performance
- Performance is related to the complex mixture of hydrocarbons

Gasoline Specifications- ASTM D4814

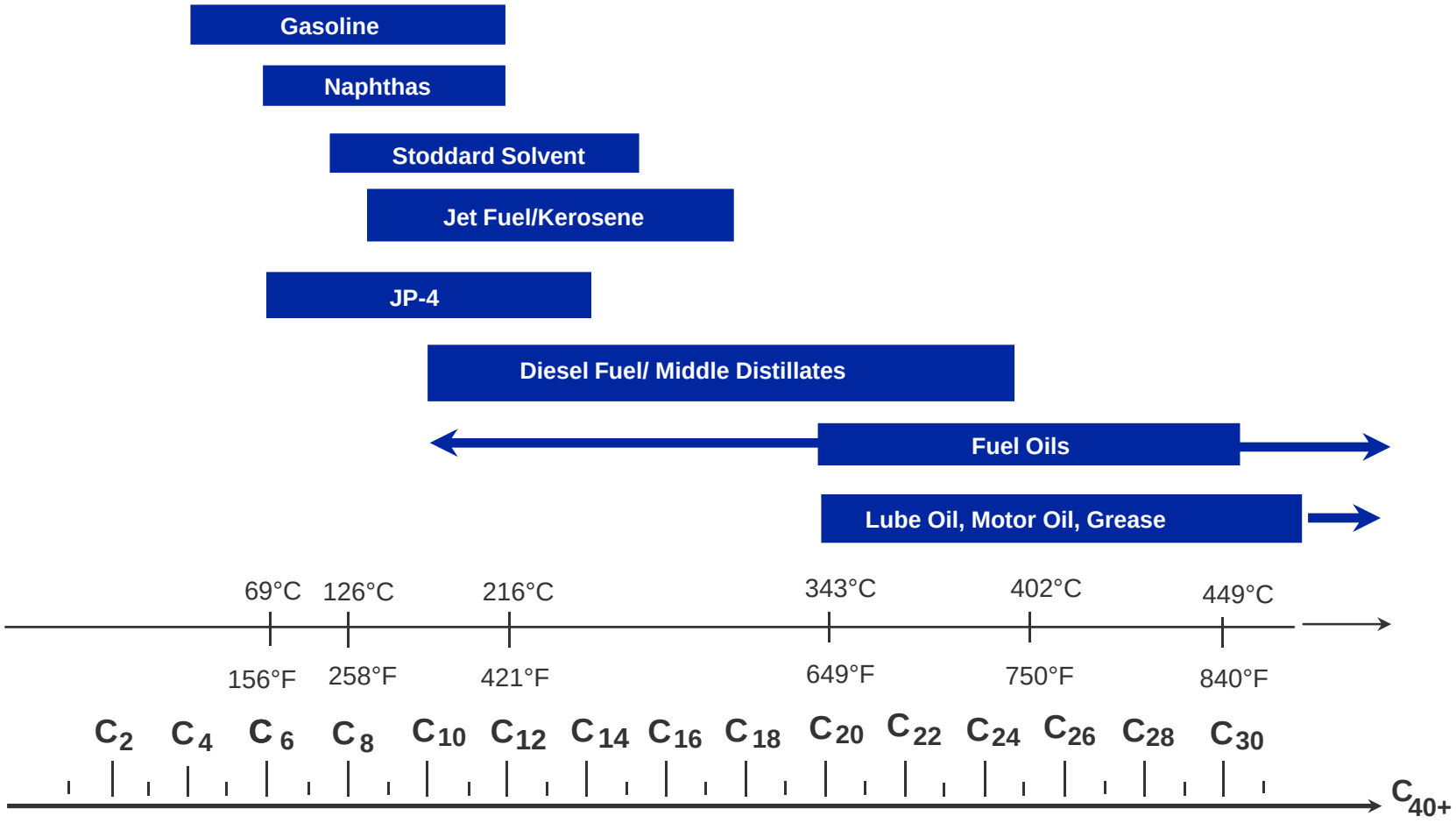
- Prior to Federal RFG and CARB, gasoline was typically blended to meet octane, RVP and distillation specifications
  - Reformulated (RFG) gasoline reduced RVP and added oxygenate, benzene and aromatics specifications for targeted air basins
  - CARB gasoline went further by added specifications for sulfur, olefins, and more stringent distillation requirements for California
- Emerging requirements – EPA Tier II and CARB Phase 3 (Pharmaceutical Grade Gasoline!)
  - Further reduction in sulfur and benzene specifications
  - Ethanol addition driven by renewable legislation

Chemistry: Desire streams with iso-paraffins, naphthenes, toluene (non-benzene aromatic), and olefin molecules within limits, manage challenge of ethanol addition, minimize low octane normal paraffins

Source Identification of Gasoline-Gasoline Blending Components

- Distillation - light straight run
- Cracking
  - Thermal - Coker light naphtha
  - Catalytic - FCC light naphtha
  - Hydro - Isomaxate
- Alkylation - Alkylate
- Reforming - reformate

Approximate Carbon and Boiling Ranges of Petroleum Products



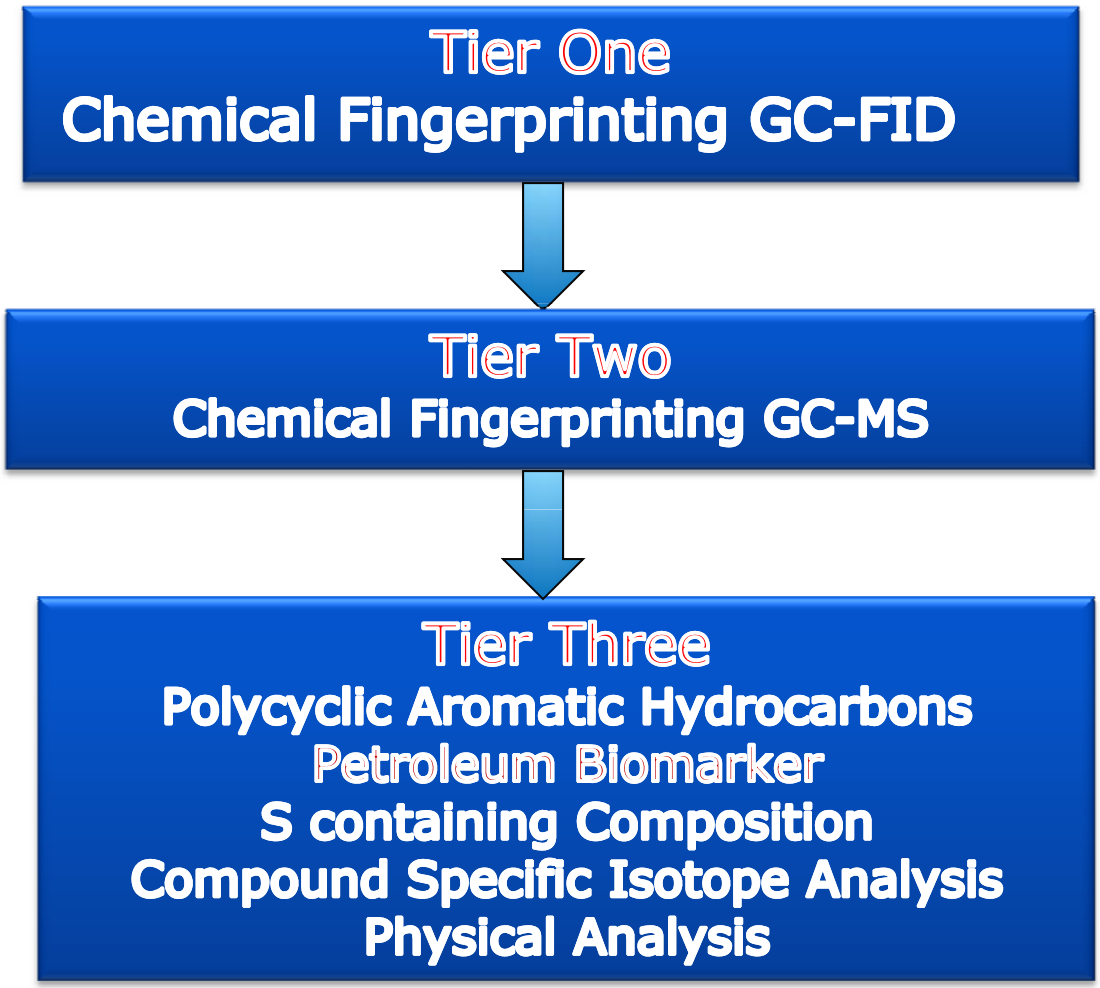
Diesel Fuel Oils by ASTM D975

Diesel Fuel Class	Specification
No. 1-D S15	Special Purpose, Light middle Distillate UL Diesel S< 15ppm
No. 1-D S500	Special Purpose, Light middle Distillate UL Diesel S< 500 ppm
No. 1-D S5000	Special Purpose, Light middle Distillate UL Diesel S< 5000 ppm
No. 2-D S15	General Purpose, Light middle Distillate UL Diesel S< 15ppm
No. 2-D S500	General Purpose, Light middle Distillate UL Diesel S< 500 ppm
No. 2-D S5000	General Purpose, Light middle Distillate UL Diesel S< 5000 ppm
No. 4-D	A heavy distillate/Blend distillate/Residual Oil

What are in Our Tool Boxes for source identification?

- Refining Technology/Composition Changes
- Star-gram- Pattern Recognition based on composition analysis
- PAH distribution-double ratio plot
- Biomarker Analysis for Diesel/Crude Oil
- Bulk Stable Isotope Ratio Mass Spectrometry and CSIA-MS (Compound Specific Isotope Analysis Mass Spectrometry)
- Multidimensional GCxGC
- Multivariate statistical analysis

Tiered Approach to Fingerprint oils in Environmental Forensic



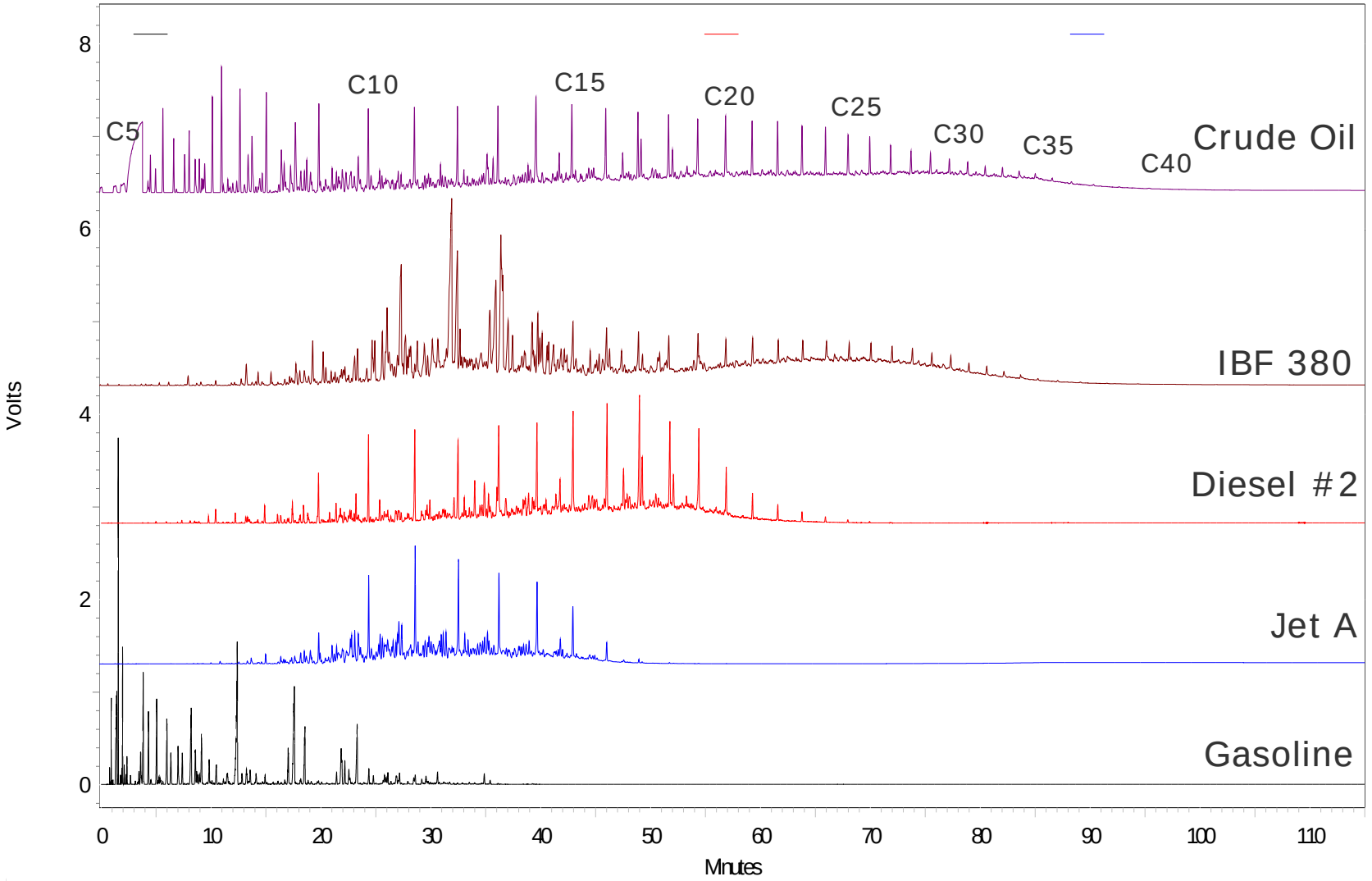
D3328
D6729
8015

D5739
8260/8270

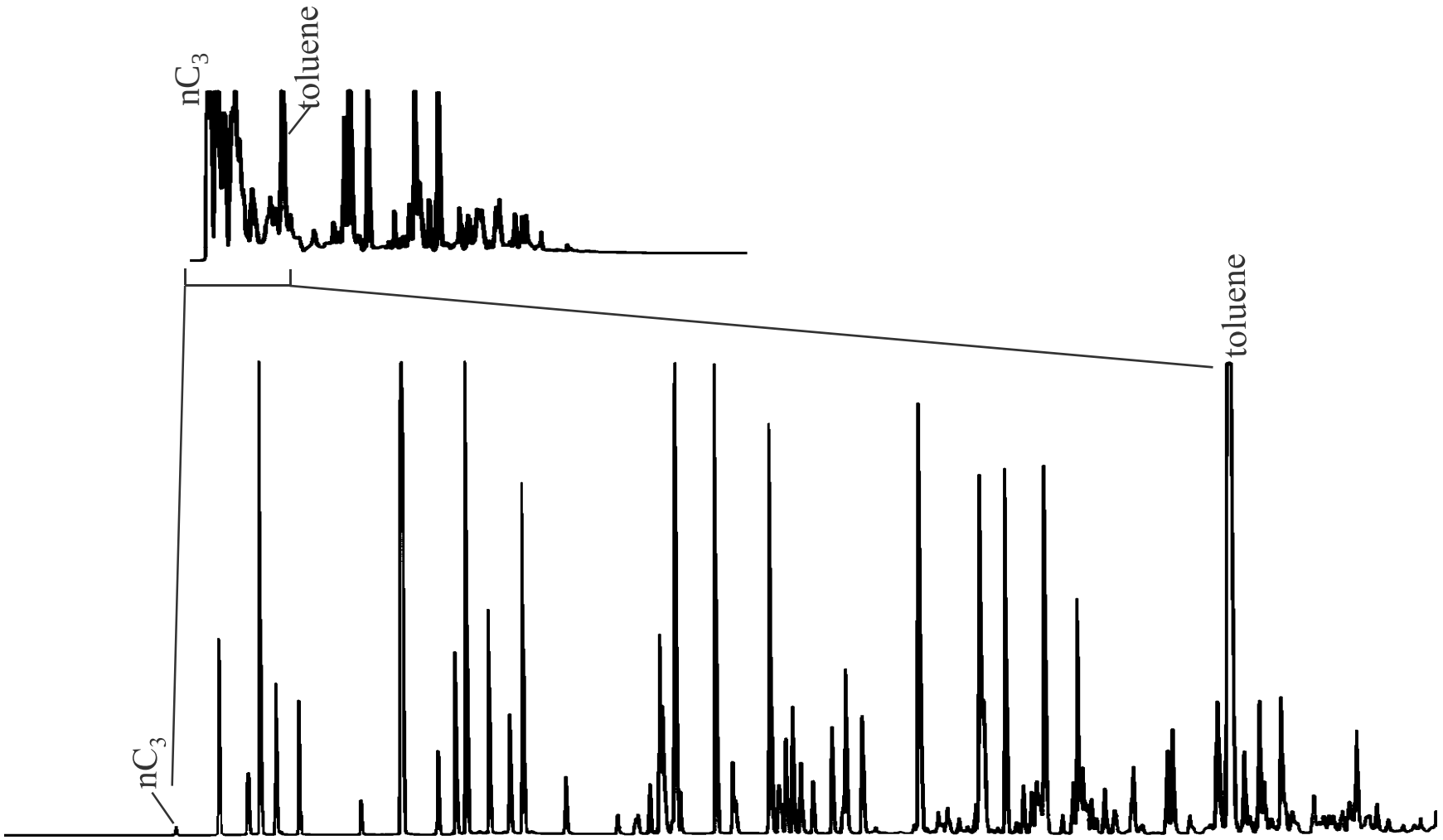
Comparison of the Fingerprinting Methods

- Both ASTM D3328-Standard Test Methods for comparison of waterborne Petroleum Oils by GC and D5739-Oil spill identification by GC and positive ion electron impact low resolution Mass spectrometry was introduced in 1995 are not suitable for Gasolines.
- Both ASTM D3288 and D5739 are Semi-quantification though D5739 will provide the normalized histogram for the distribution of class of components.
- D6729 Gasoline composition analysis with High Resolution GC only suitable for gasoline. EPA 8260 also could be used as the PIANO analysis.
- 8015m and 8270C modification came from ASTM 3328 in 1974. Polyaromatic hydrocarbon and Biomarker could be added into 8270 test matrix with proper standards.

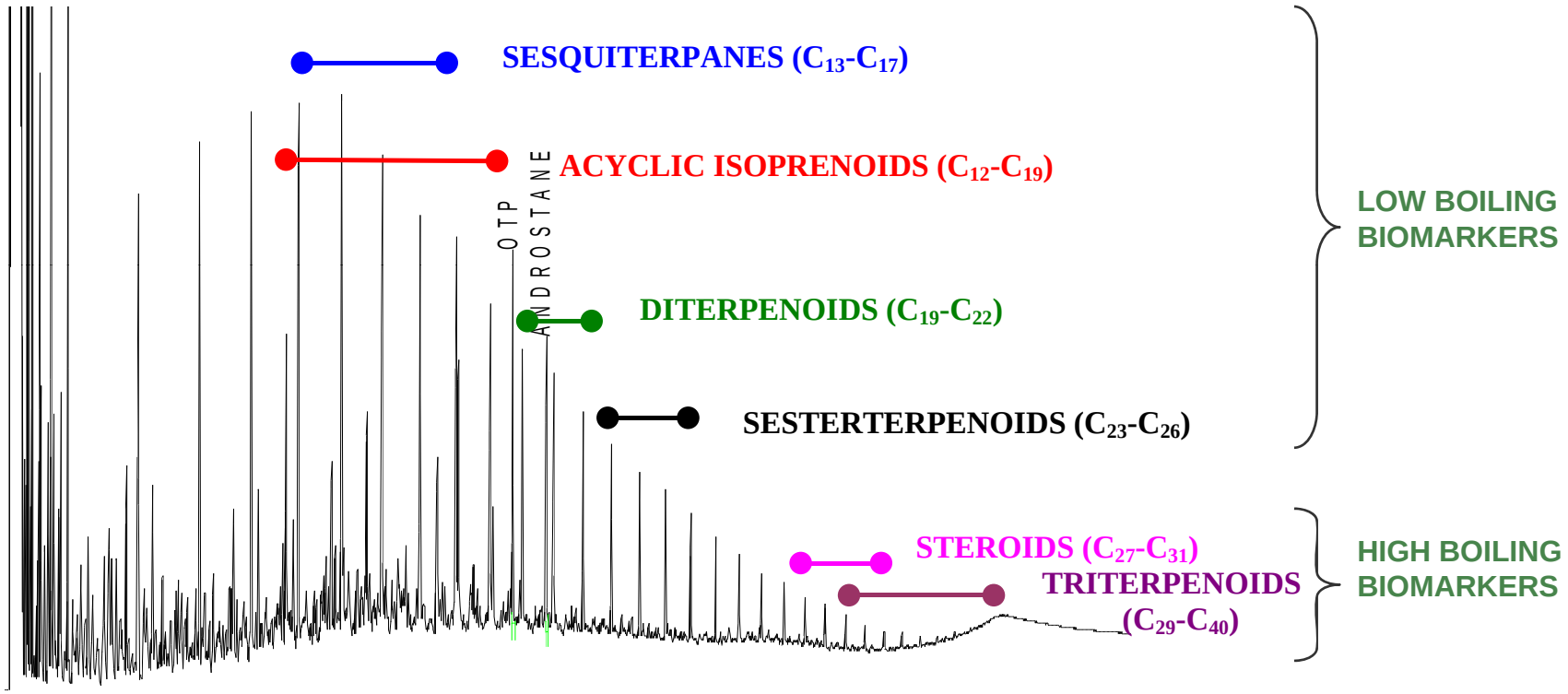
Qualitative Assessment by GC-FID-depends on DQO (Data Quality Objective)



Modified 8015 vs. Detailed Hydrocarbon Analysis D6729 (DHA method for gasoline composition analysis)



Biomarkers in Petroleum Hydrocarbons



GASOLINE/HEAVY NAPHTHA

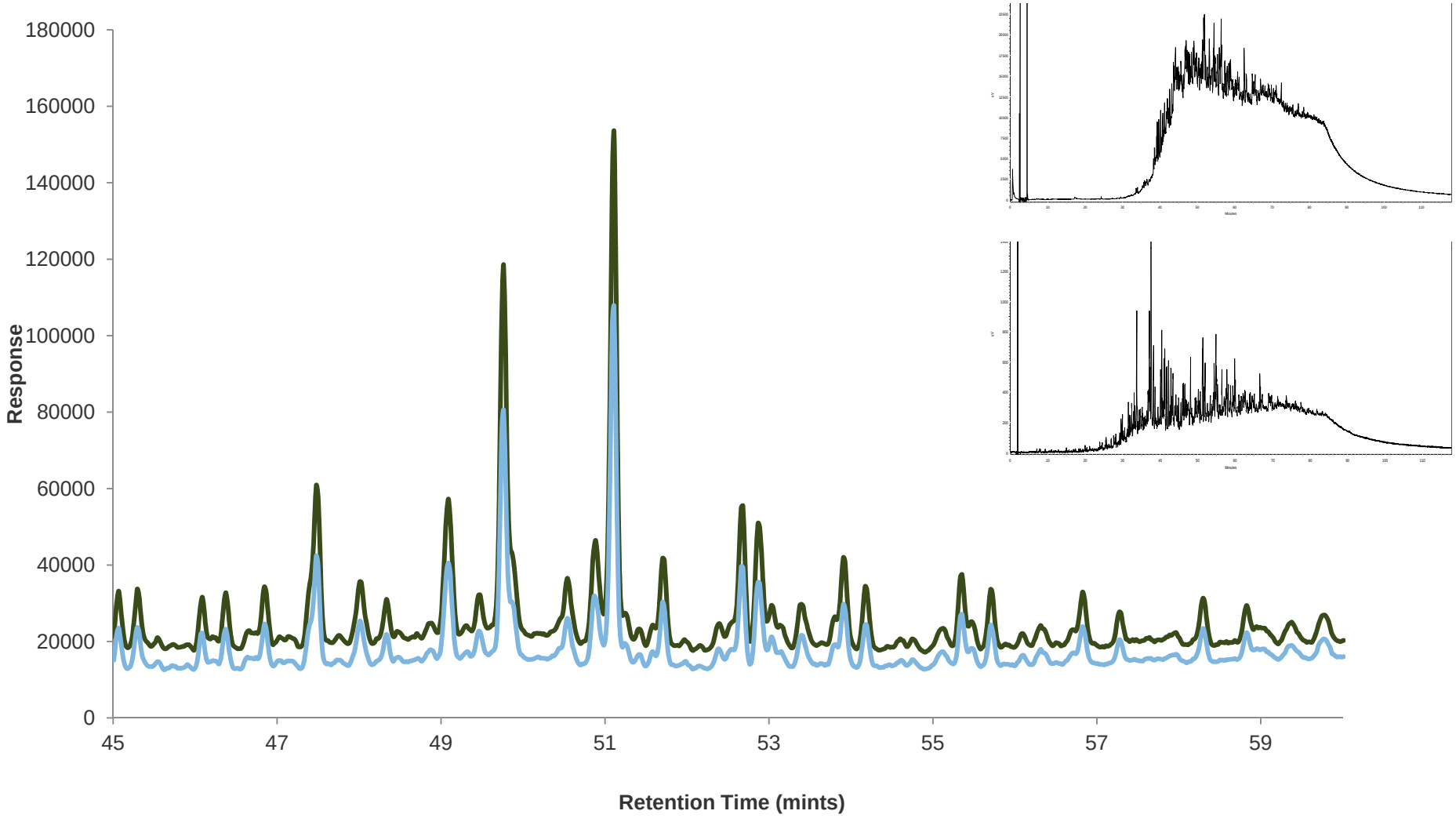
KEROSENE-JET A-DIESEL #1

DIESEL FUEL #2/FUEL OIL #2

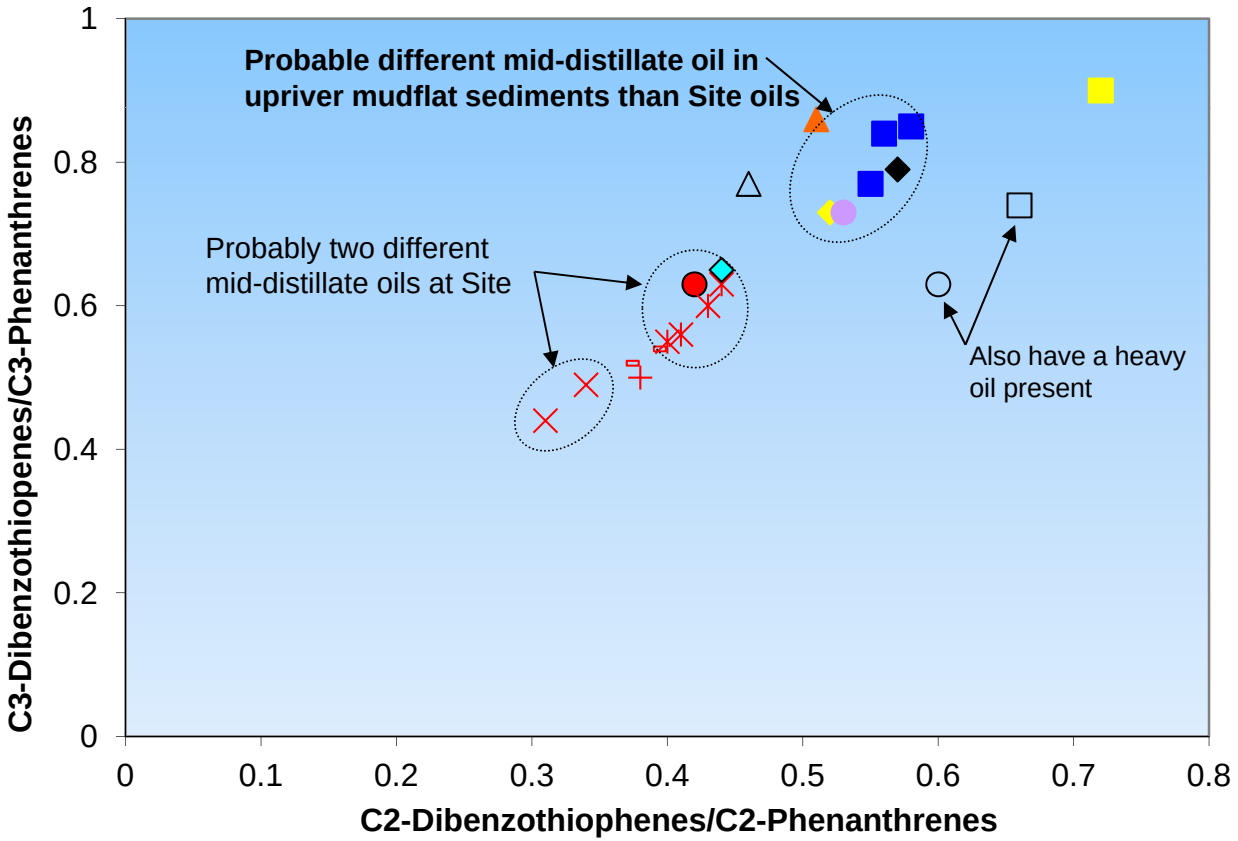
BUNKER C/FUEL OIL#6

ENGINE/LUBE OILS

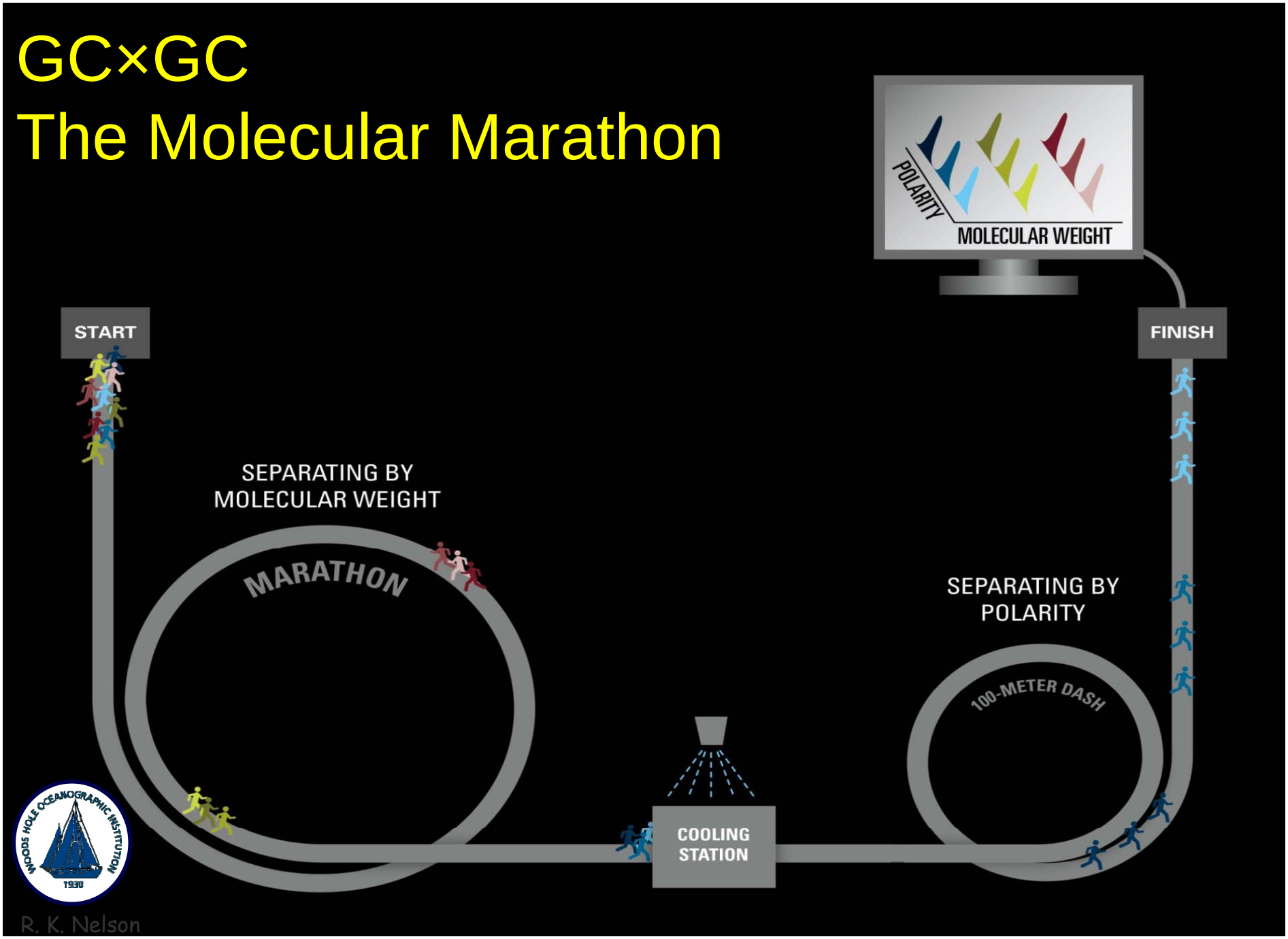
Biomarkers provide additional evidence when dealing with biodegraded products-m/z 191 tricyclic terpanes



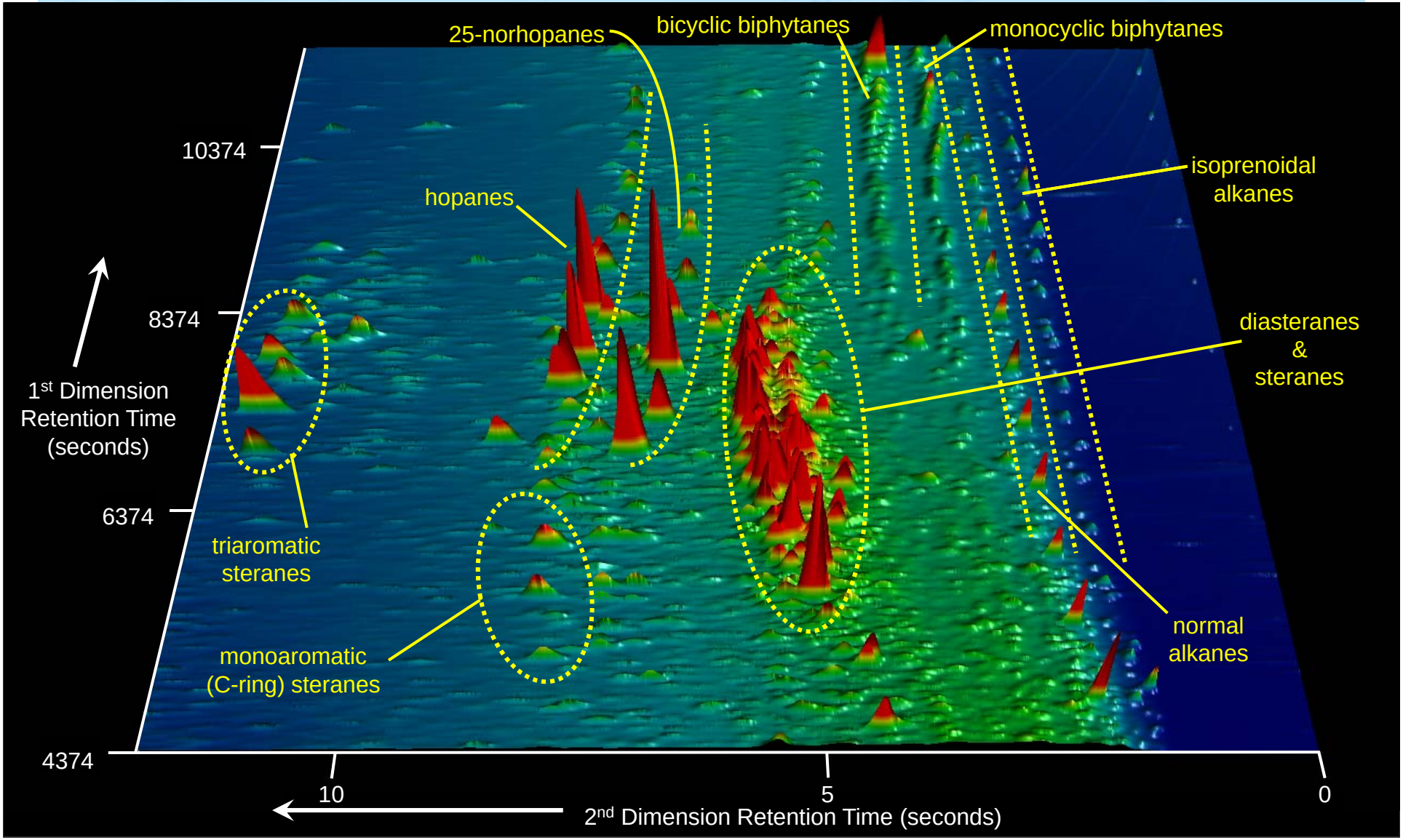
Diagnostic Ratio originated from different classes of component to correlate the source

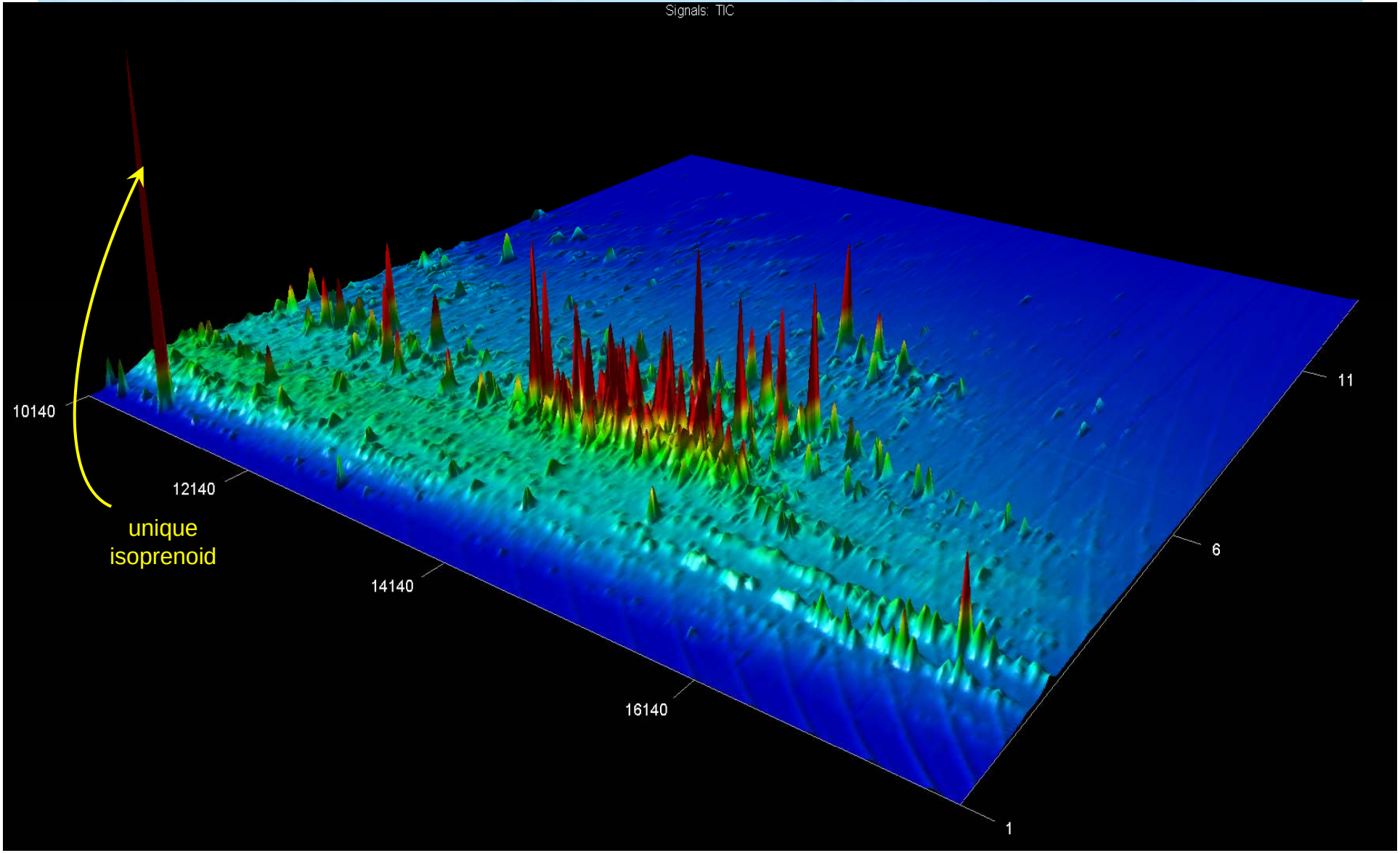


GC×GC
The Molecular Marathon

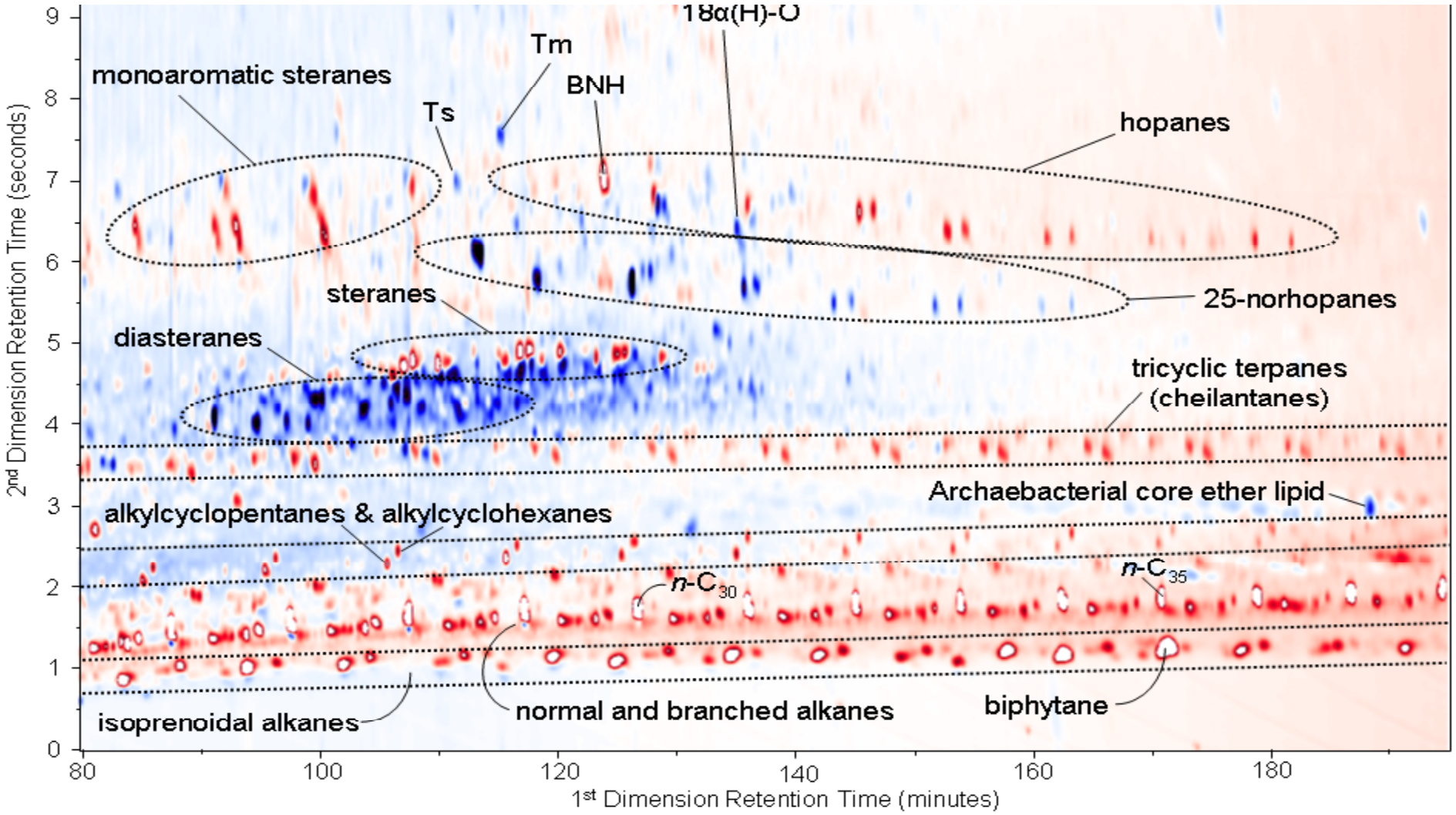


Multidimensional Biomarker Separation





Difference Chromatogram



Interpretation of fingerprinting data is not always easy

- **Broad range of fuel specifications**
- no product is sold as molecules, specifications are based on performance -octane number, V/L (vapor/liquid) and regulations -RVP (Reid vapor pressure), Benzene
- Limits on total olefins, aromatics, Lead, Sulfur, and MTBE are recent regulation
- **Weathering**
  - Evaporation
  - Biodegradation
  - Oxidation
  - sorption
- **Mixtures of products and sources**

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Q&A