



# Hydrocarbon Delineation in Muskeg: Distinguishing Biogenic from Petrogenic Sources

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# Outline of Presentation

- Introduction and Challenges in Muskeg Environments
- Clients Objectives and Analytical Approach
- Soil Physical-Chemical Characteristics (Box Plots)
- GC-FID and GC-MS Chromatograms
- \*Approach to Establish *True* Biogenic Source
- Recommended Analytical Program and Corrections for Biogenic Input

# Introduction & Objective

Upstream emulsion flow line rupture releasing a saline, sour crude into a low lying muskeg setting in NE British Columbia.

Containment and Recovery

Conductivity Survey with Soil Investigations

Regulatory Agencies

## – Challenging Environments

- Access challenges
- Analytical challenges

## – Client Objectives

- Distinguish and quantify biogenic influences
- Analytical program to facilitate delineation

# Analytical Approach

Primary analytical methods -

- GC-FID analysis of hexane/acetone extract (EPH)
  - Fraction quantified: C<sub>10</sub>-C<sub>19</sub> and C<sub>19</sub>-C<sub>32</sub>
- GC-FID analysis of silica gel EPH extract
- GC-MS Open Characterization
  - Carbon Preference Index (CPI)
  - Unresolved Complex Mixture (UCM)

Considered, but not used -

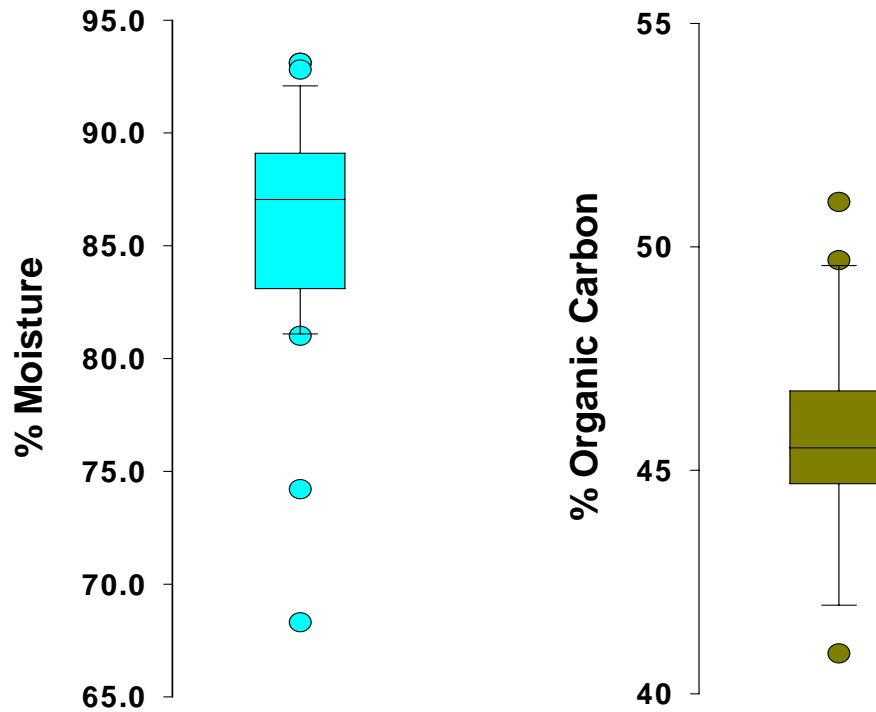
- Aromatic vs. Aliphatic Fractionation
- GC-MS Library
- Isotopic Ratios and Biomarkers

# Supporting Literature – CPI/UCM

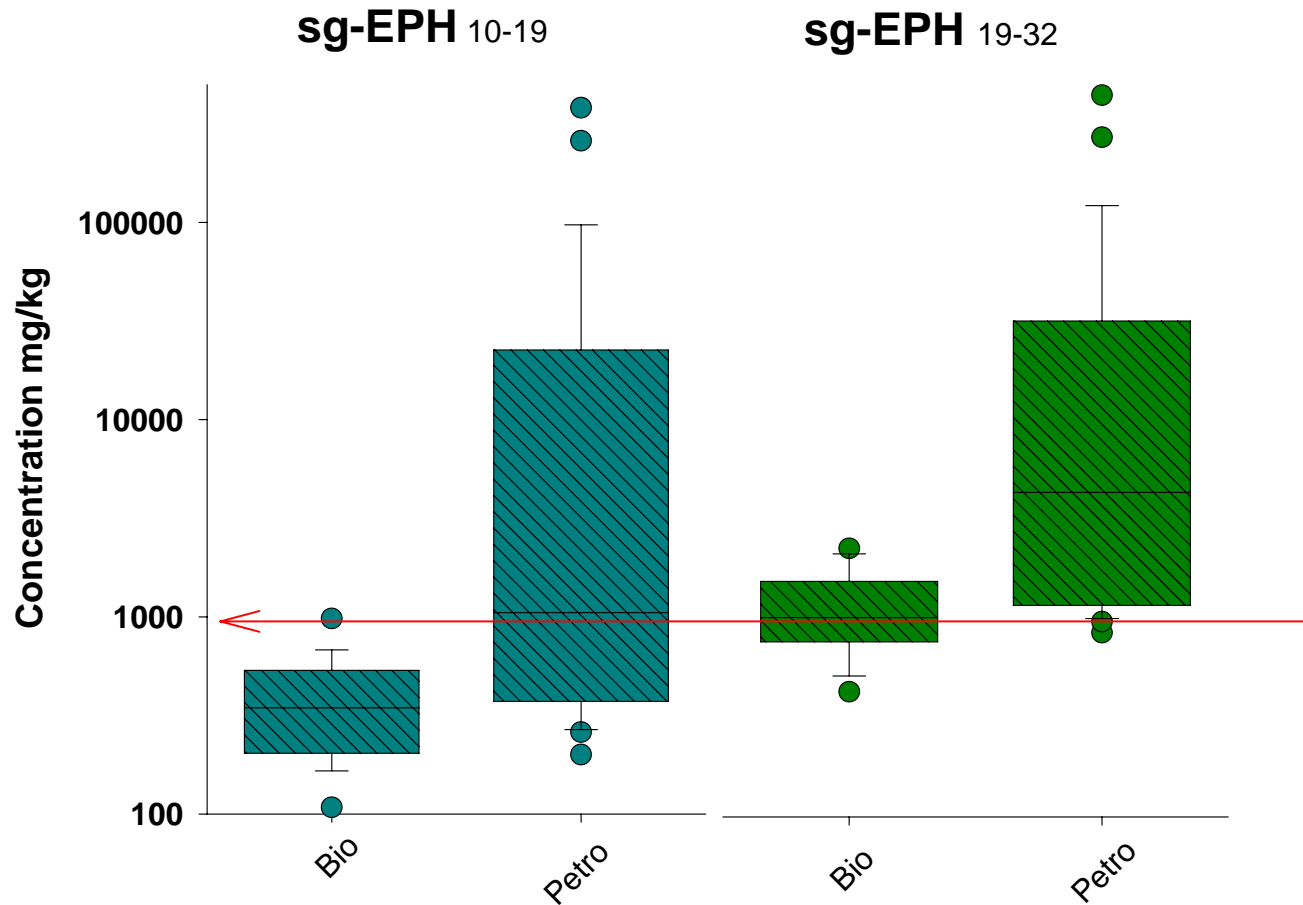
Studies on Distribution and Origin of Hydrocarbons in Estuary Sediment.

- J. Colombo et al. (1989)
  - Use of *n*-alkane (CPI) and PAH distribution indexes in Rio de La Plata Estuary, Argentina.
- V. Choiseul et al. (1998)
  - Use of UCM and CPI to study the distribution of hydrocarbons in the Liffey Estuary, South – West Irish Coast
- K. Tran et al.
  - Use of *n*-alkane ratios (CPI), UCM and various PAH ratios to determine petrogenic from biogenic sources off San Diego, USA

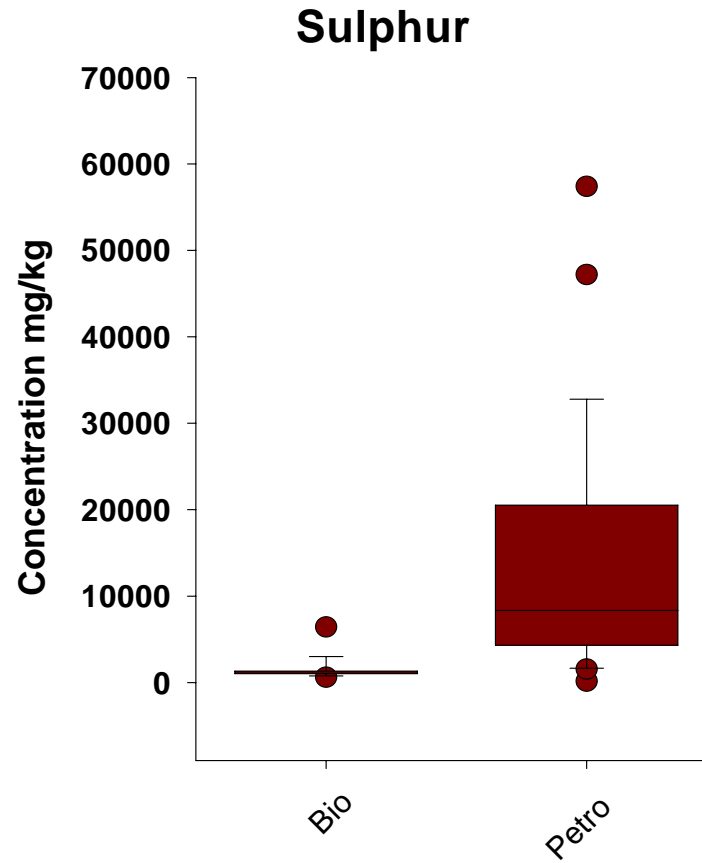
# Peat Soil – High Moisture and Organic Carbon



# Silica Gel Extractable Petroleum Hydrocarbons



# Sulphur Concentration

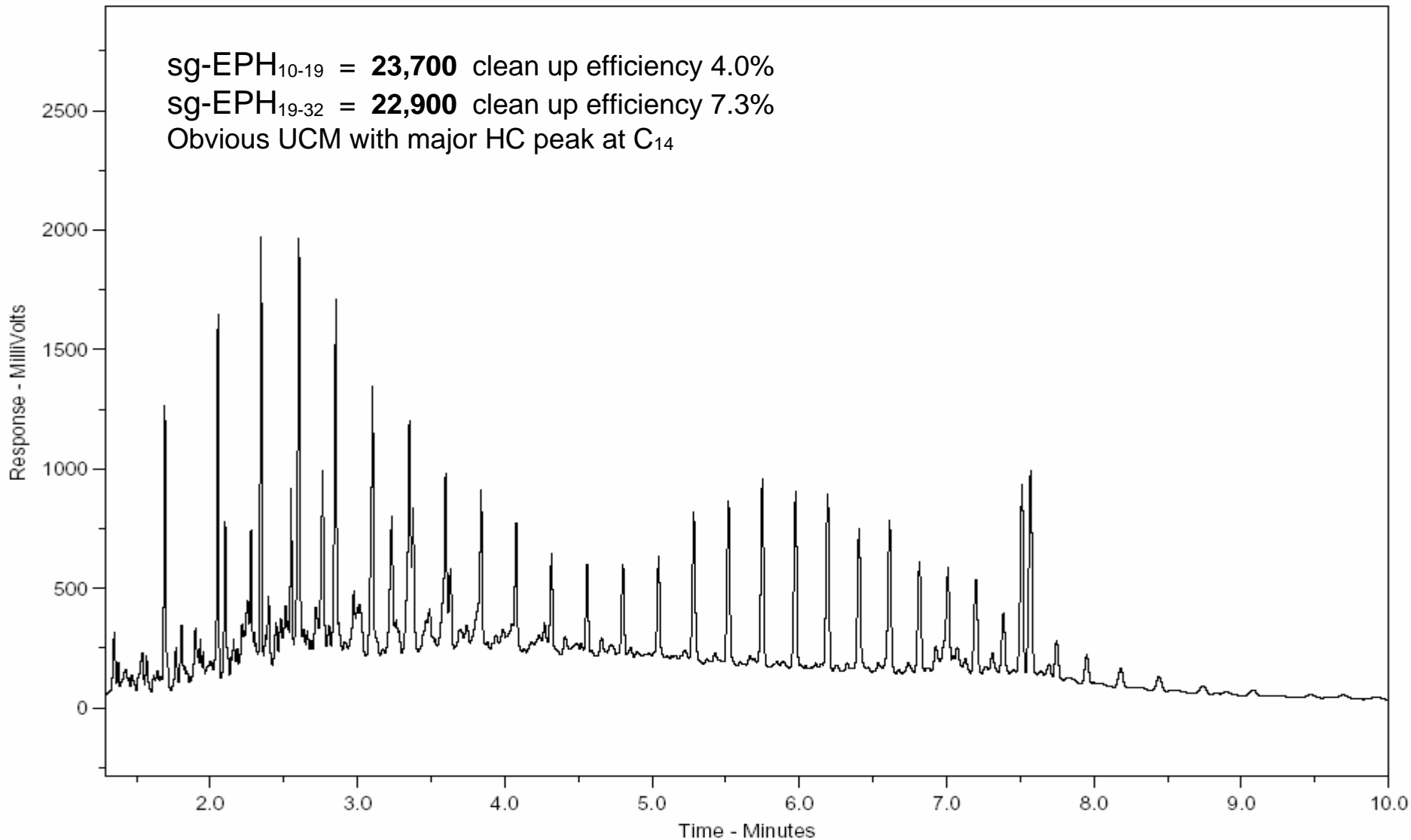


# GC-FID Chromatogram for Petrogenic Source

sg-EPH<sub>10-19</sub> = **23,700** clean up efficiency 4.0%

sg-EPH<sub>19-32</sub> = **22,900** clean up efficiency 7.3%

Obvious UCM with major HC peak at C<sub>14</sub>

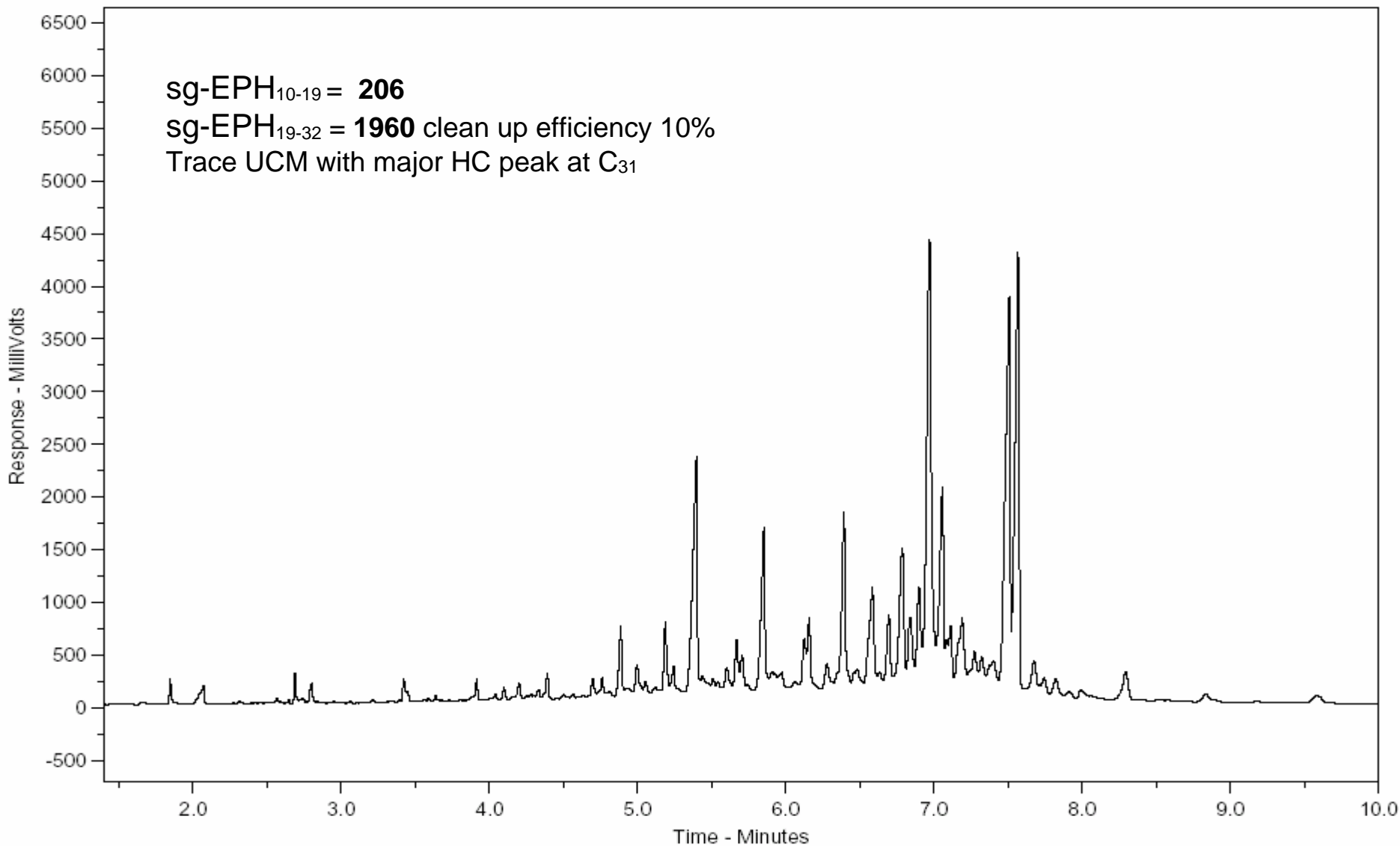


# GC-FID Chromatogram for Biogenic Sample

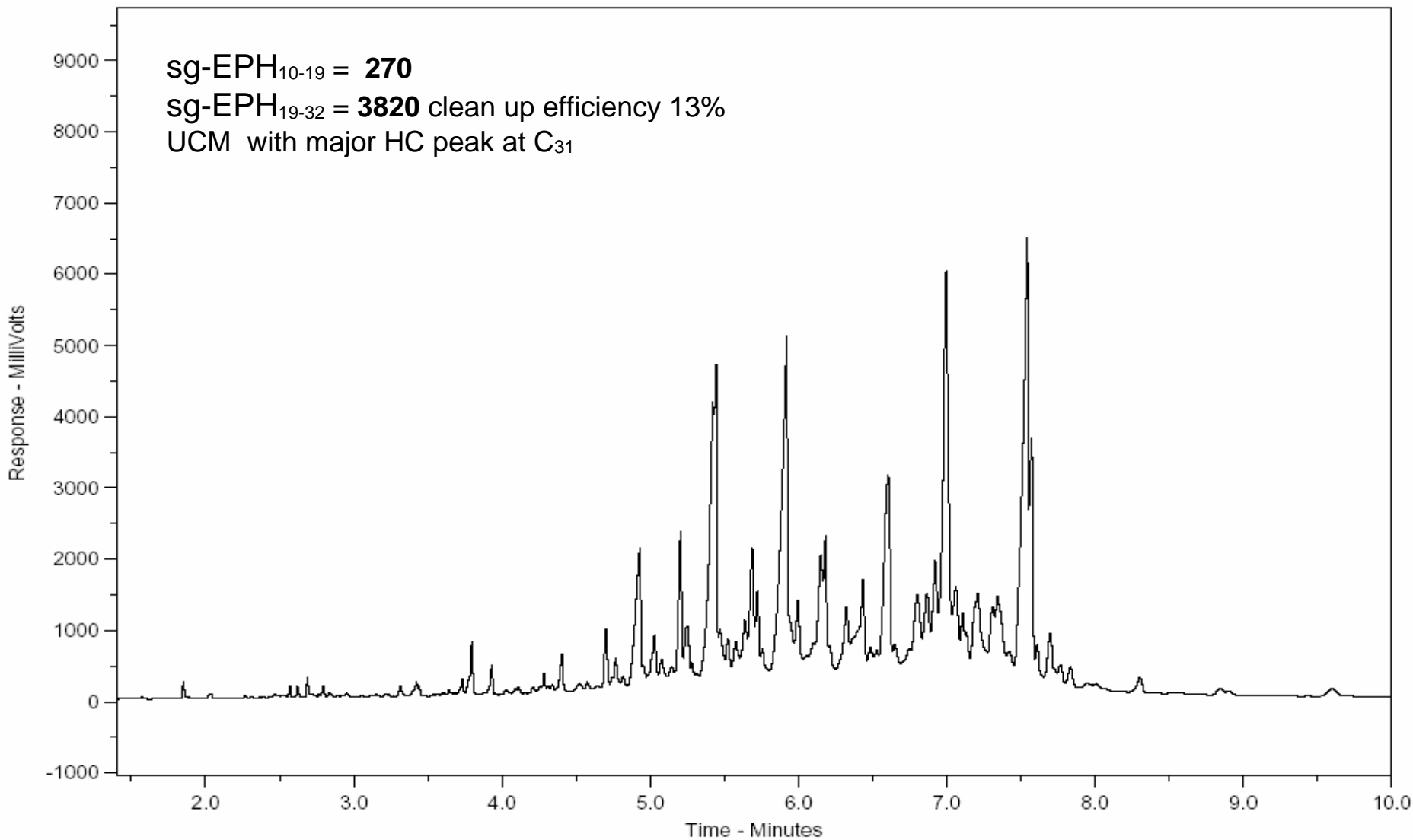
sg-EPH<sub>10-19</sub> = 206

sg-EPH<sub>19-32</sub> = 1960 clean up efficiency 10%

Trace UCM with major HC peak at C<sub>31</sub>

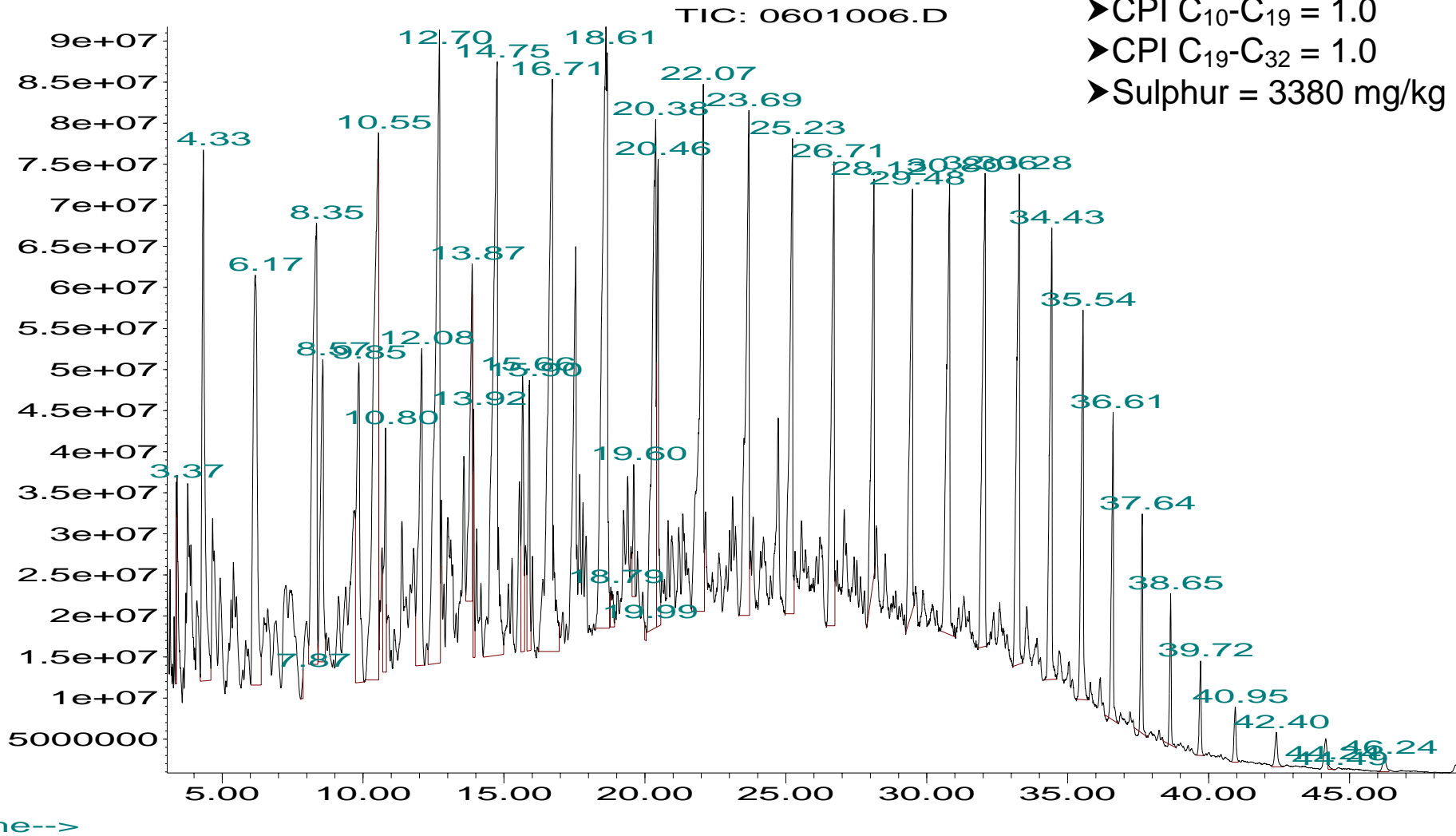


# GC FID Chromatogram for Biogenic -Petrogenic Mix



# GCMS Total Ion Chromatogram: Petrogenic Source

Abundance

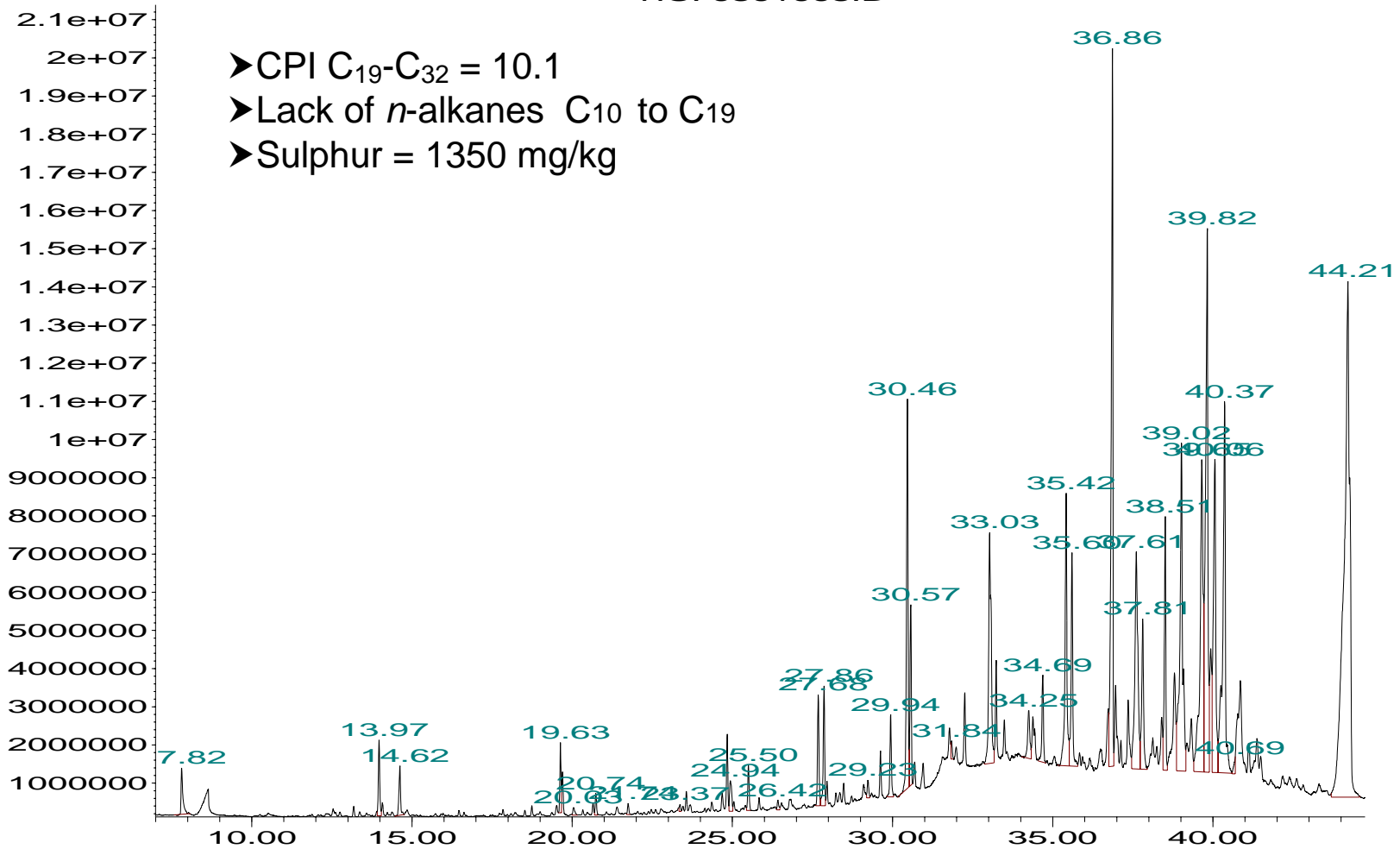


- CPI C<sub>10</sub>-C<sub>19</sub> = 1.0
- CPI C<sub>19</sub>-C<sub>32</sub> = 1.0
- Sulphur = 3380 mg/kg

# GCMS Total Ion Chromatogram: Biogenic Sample

Abundance

TIC: 0501005.D



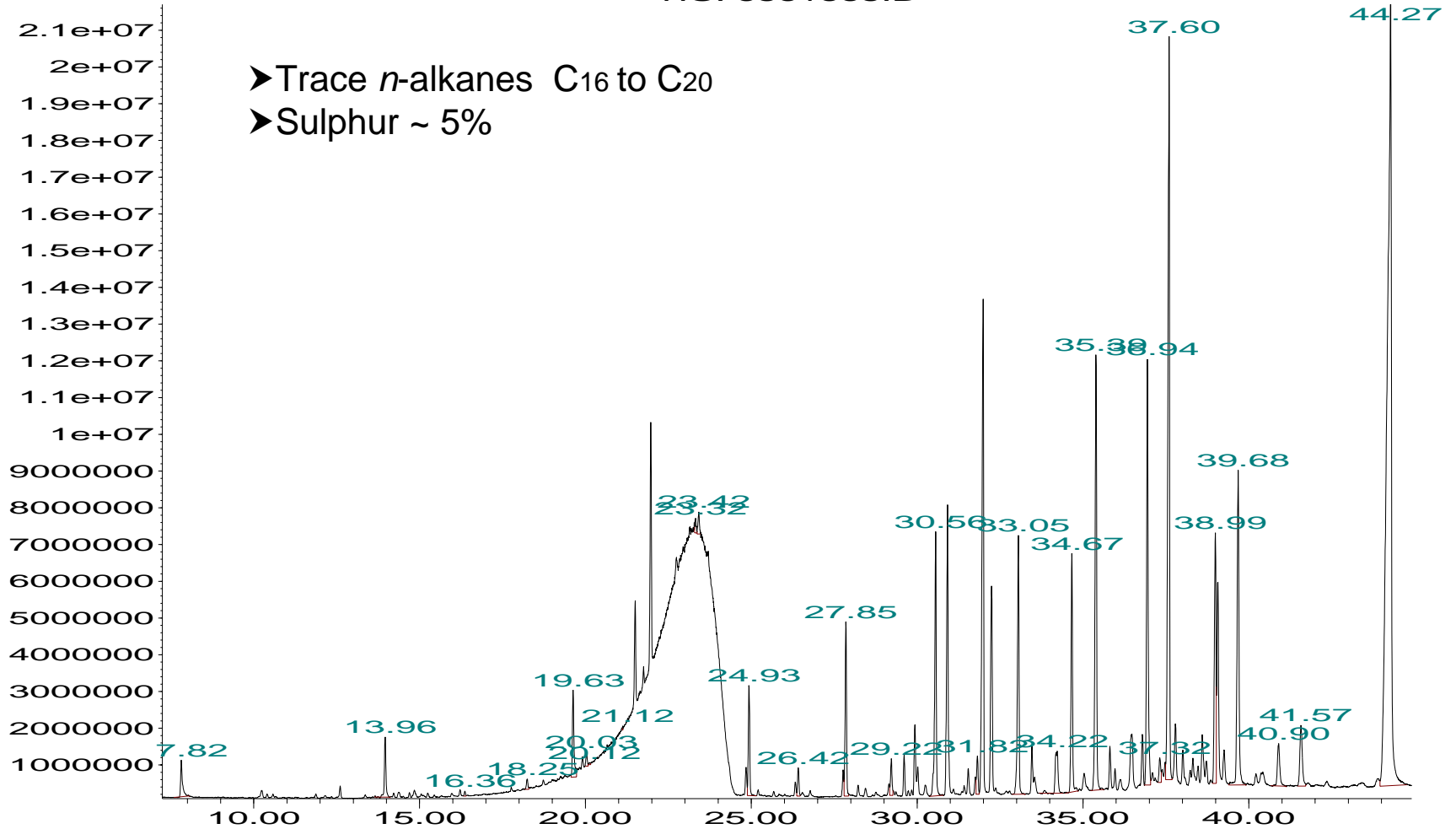
- ▶ CPI C<sub>19</sub>-C<sub>32</sub> = 10.1
- ▶ Lack of *n*-alkanes C<sub>10</sub> to C<sub>19</sub>
- ▶ Sulphur = 1350 mg/kg

Time-->

# GCMS Total Ion Chromatogram: Biogenic-Petrogenic Mix

Abundance

TIC: 0901009.D

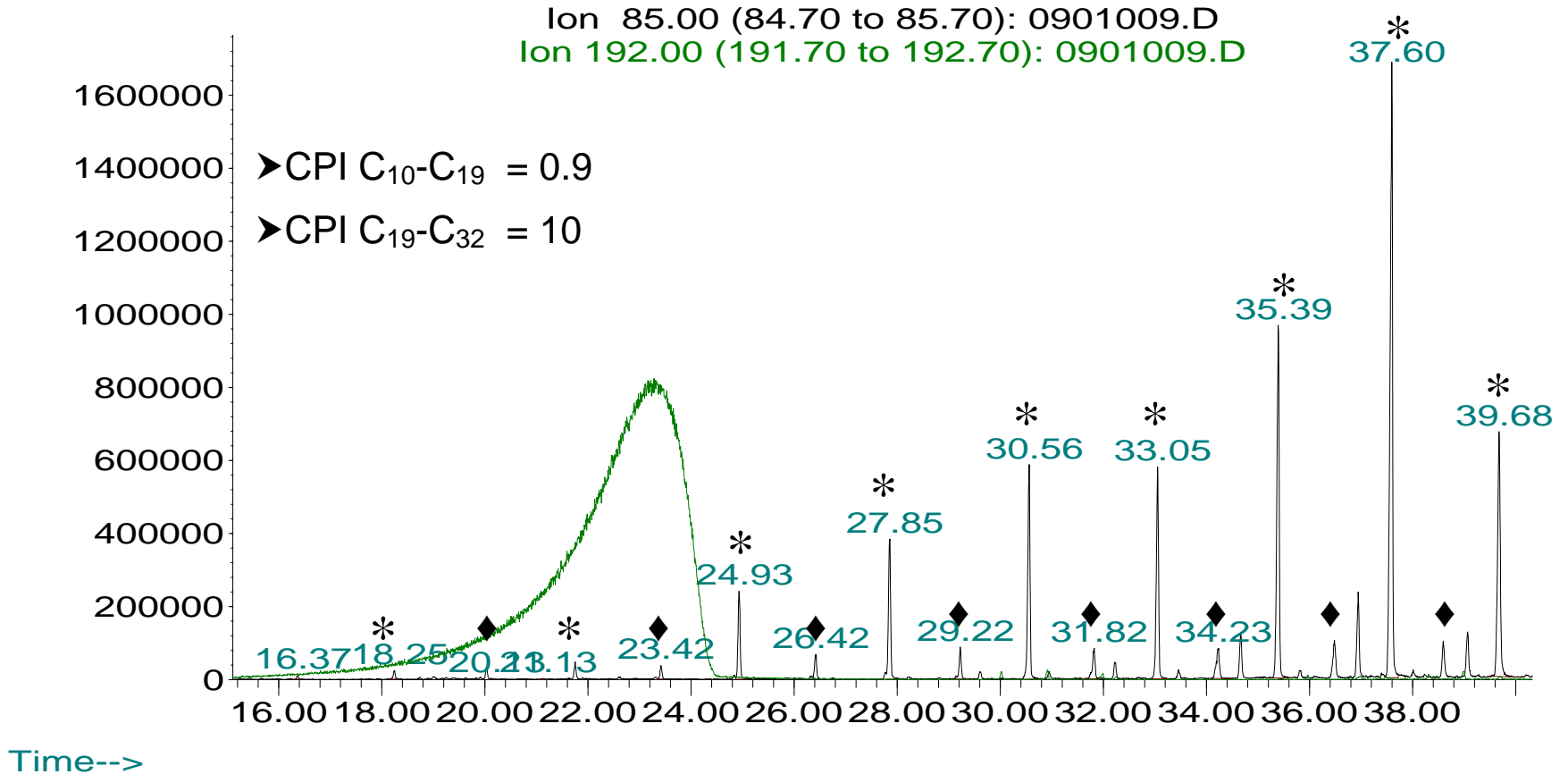


- ▶ Trace *n*-alkanes C<sub>16</sub> to C<sub>20</sub>
- ▶ Sulphur ~ 5%

Time-->

# GC-MS Scan Alkanes + Sulphur: Petrogenic-Biogenic Mix

Abundance

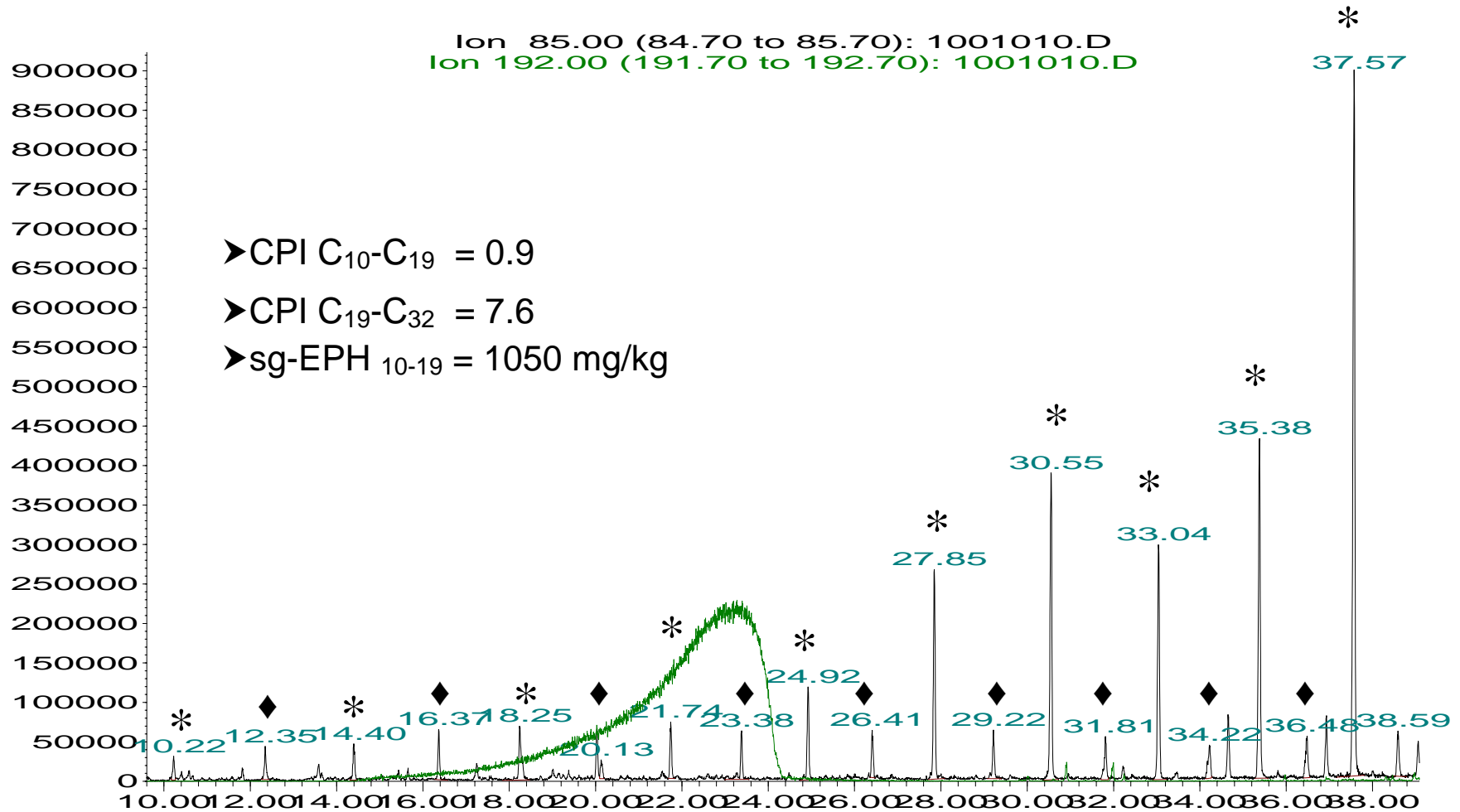


\* = odd carbon # n-alkanes

◆ = even carbon # n-alkanes

# Petrogenic-Biogenic Mix Second Example

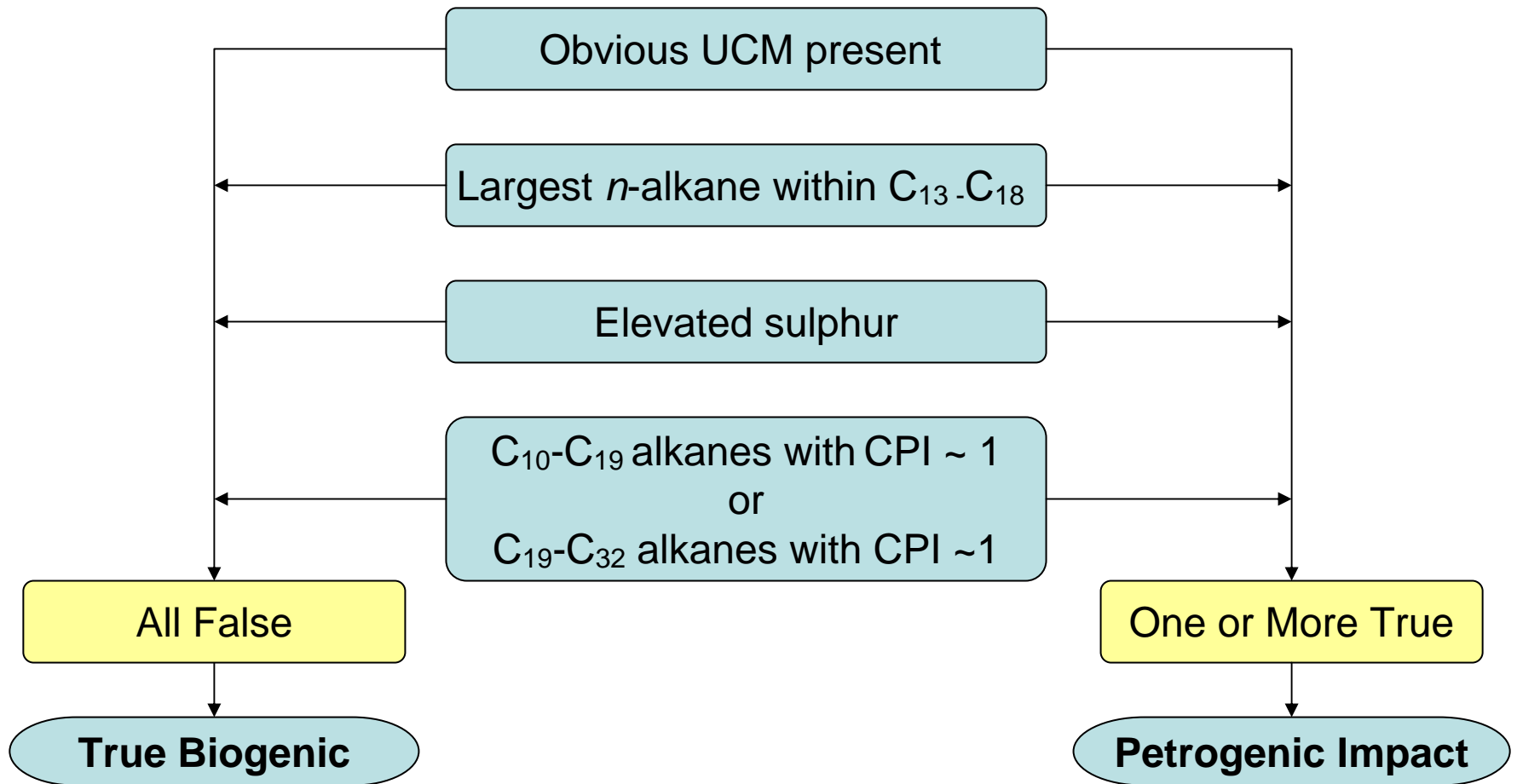
Abundance



\* = odd carbon # n-alkanes

◆ = even carbon # n-alkanes

# Determination of “*True Biogenic*” Samples



# Analytical Program and Definition of “*Contaminated Peat*”

## Analytical Program

- Organic Carbon
- Silica Gel EPH<sub>10-19</sub> and EPH<sub>19-32</sub>
- Total Sulphur

## Determination of “*Contaminated Peat*”

- sg-EPH<sub>10-19</sub> compared to BC CSR uncorrected
  - **[1000 mg/kg]**
- sg-EPH<sub>19-32</sub> compared to BC CSR with correction
  - **[2400 mg/kg]** assumes biogenic contribution ~ 1400 mg/kg
- Total sulphur compared to mean from biogenic data
  - **[1500 mg/kg]**

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