



Hydrocarbon Delineation in Muskeg: Distinguishing Biogenic from Petrogenic Sources

ESSA Remediation Technologies Symposium

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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: C₁₀-C₁₉ and C₁₉-C₃₂
- GC-FID analysis of silica gel EPH extract
- GC-MS Open Characterization
 - Carbon Preference Index (CPI)
 - Unresolved Complex Mixture (UCM)

Considered, but not used -

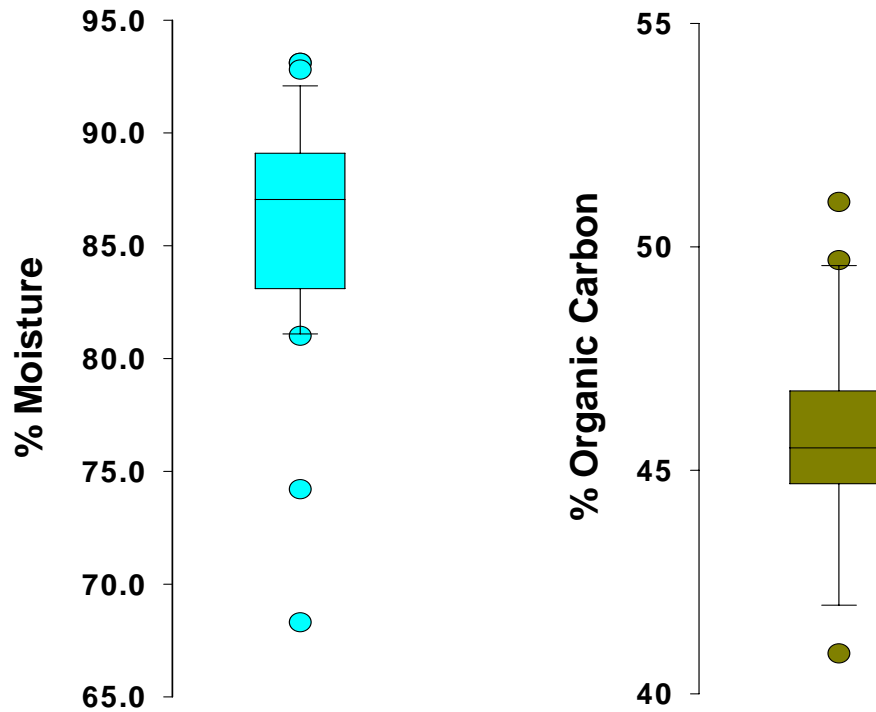
- Aromatic vs. Aliphatic Fractionation
- GC-MS Library
- Isotopic Ratios and Biomarkers

Supporting Literature – CPI/UCM

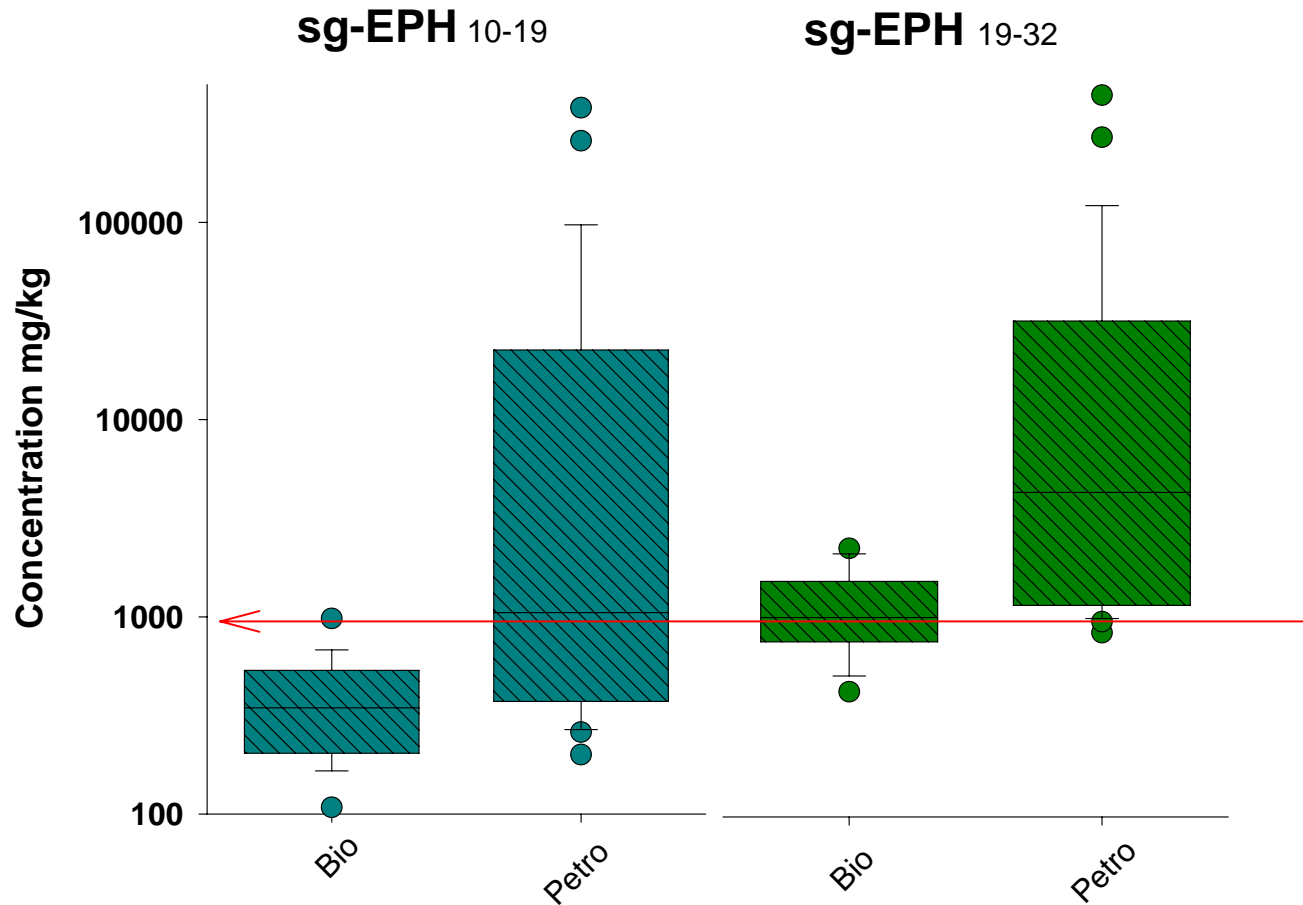
Studies on Distribution and Origin of Hydrocarbons in Estuary Sediment.

- 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

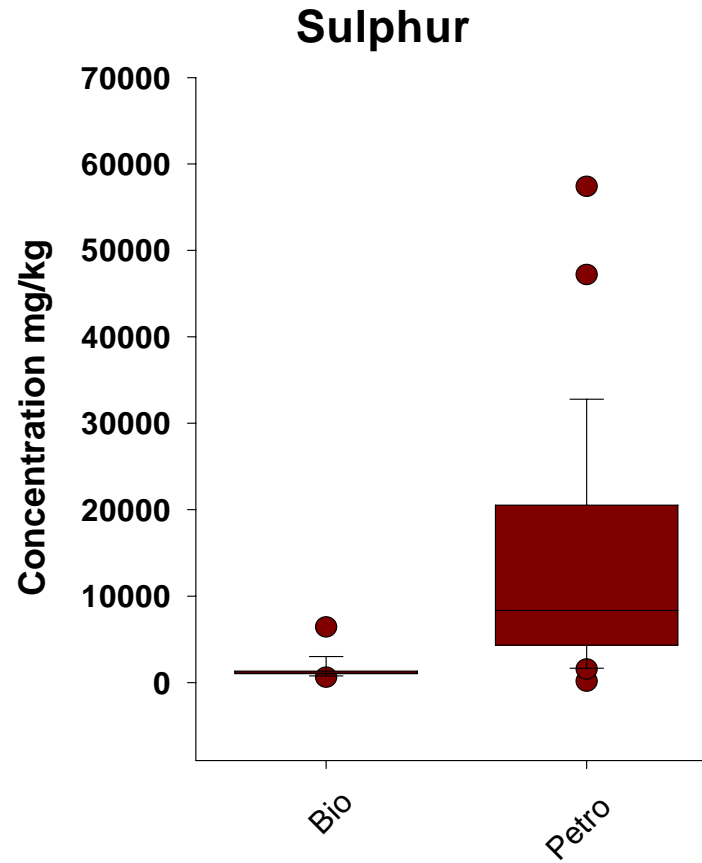
Peat Soil – High Moisture and Organic Carbon



Silica Gel Extractable Petroleum Hydrocarbons



Sulphur Concentration

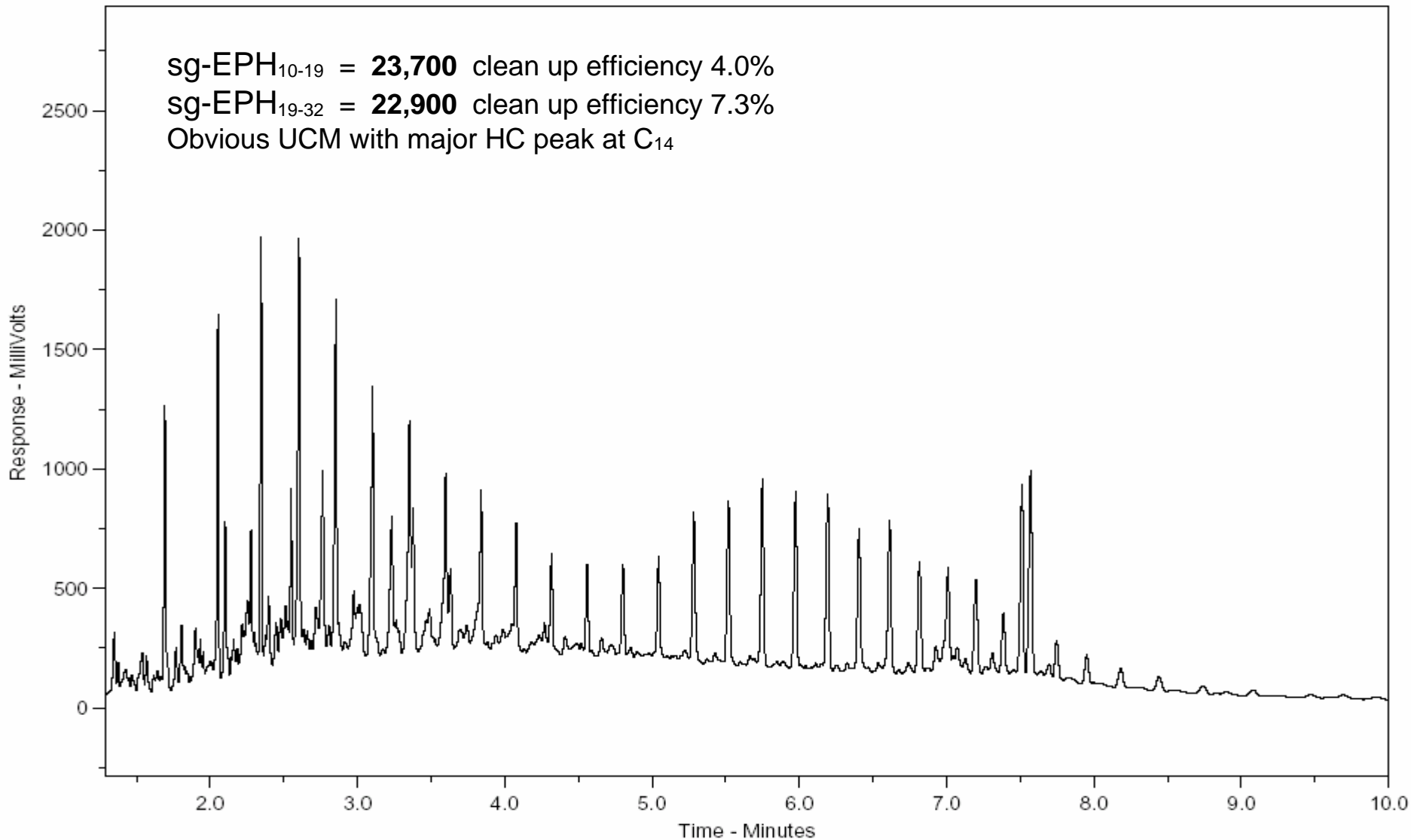


GC-FID Chromatogram for Petrogenic Source

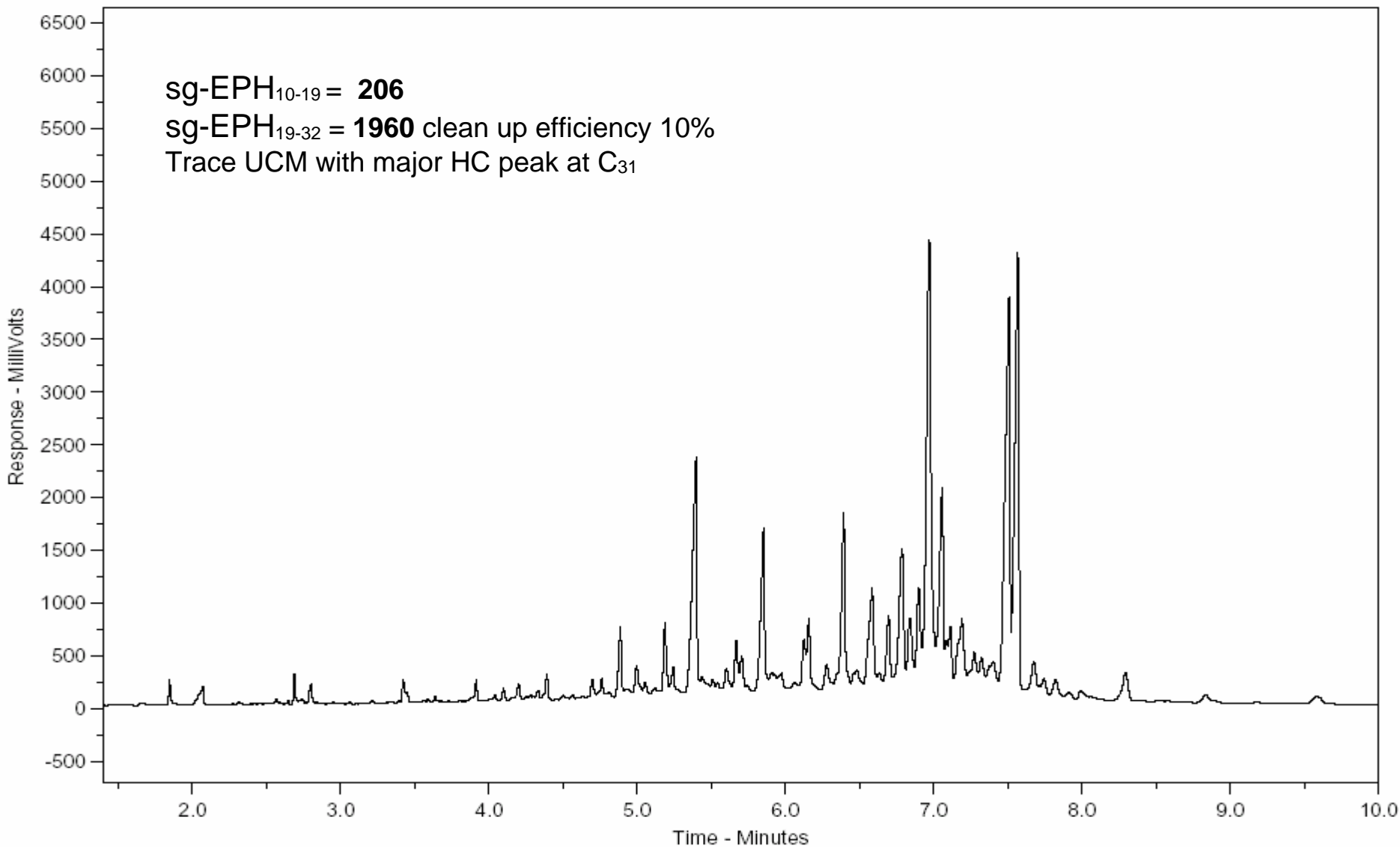
sg-EPH₁₀₋₁₉ = **23,700** clean up efficiency 4.0%

sg-EPH₁₉₋₃₂ = **22,900** clean up efficiency 7.3%

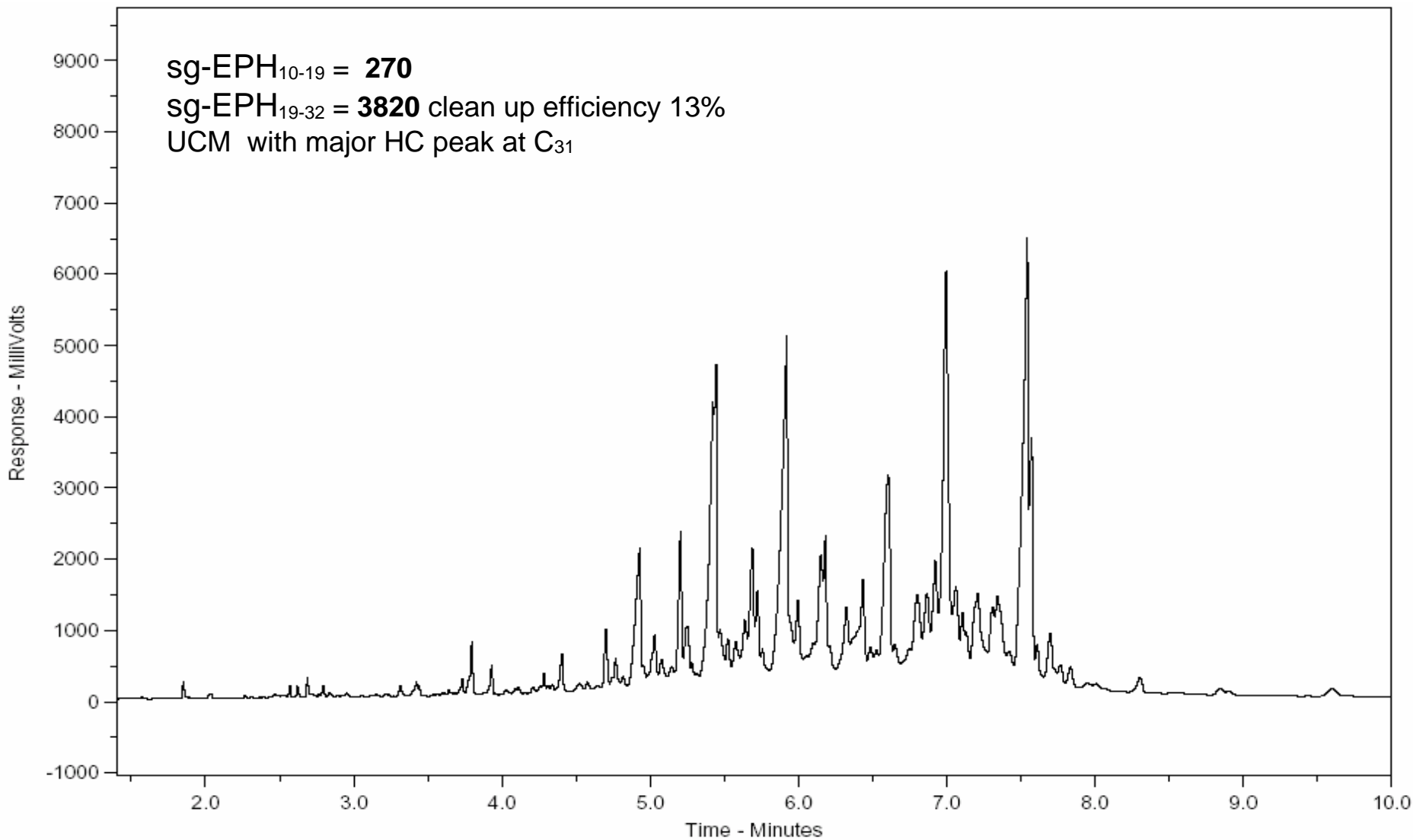
Obvious UCM with major HC peak at C₁₄



GC-FID Chromatogram for Biogenic Sample

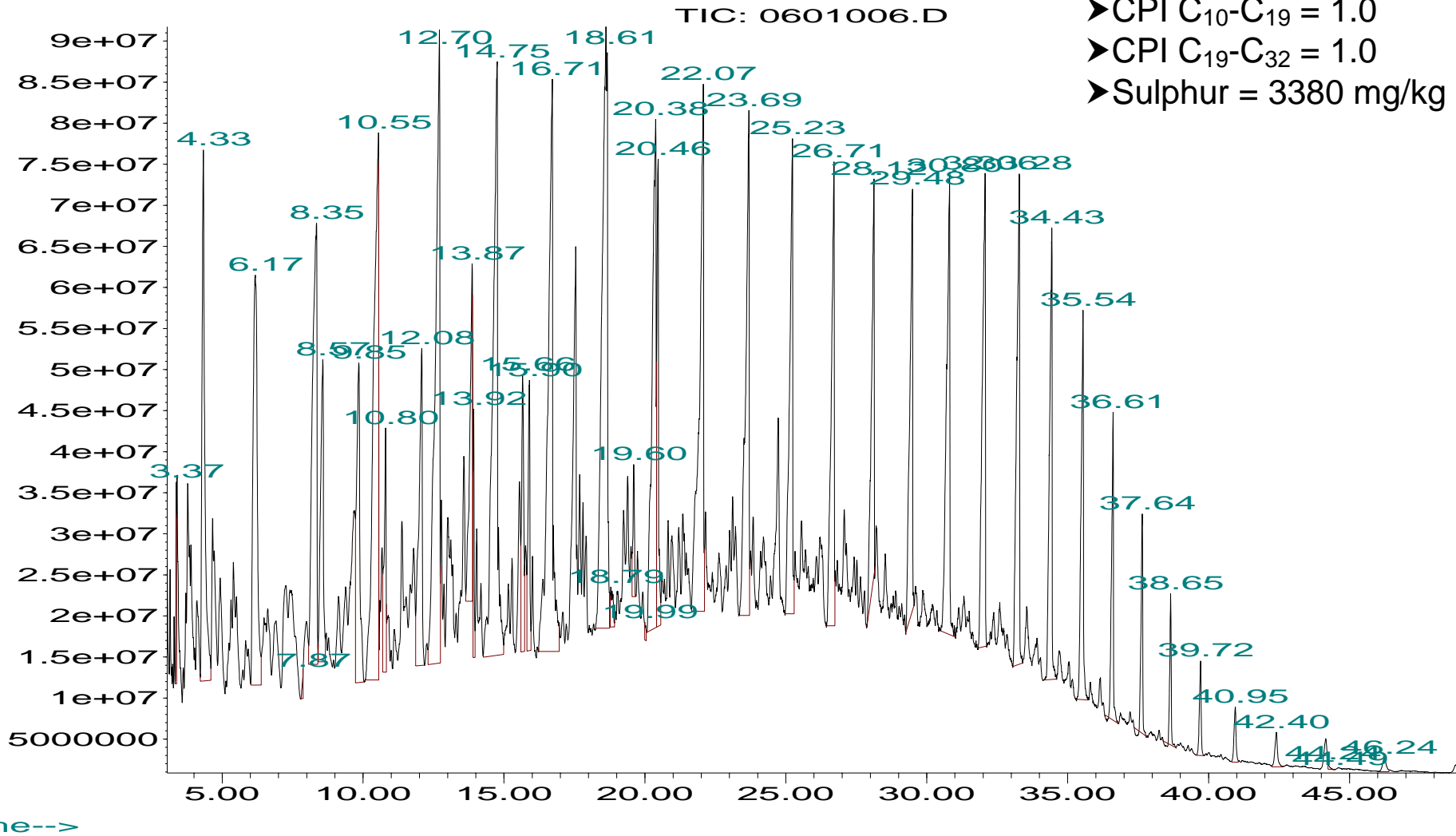


GC FID Chromatogram for Biogenic -Petrogenic Mix



GCMS Total Ion Chromatogram: Petrogenic Source

Abundance

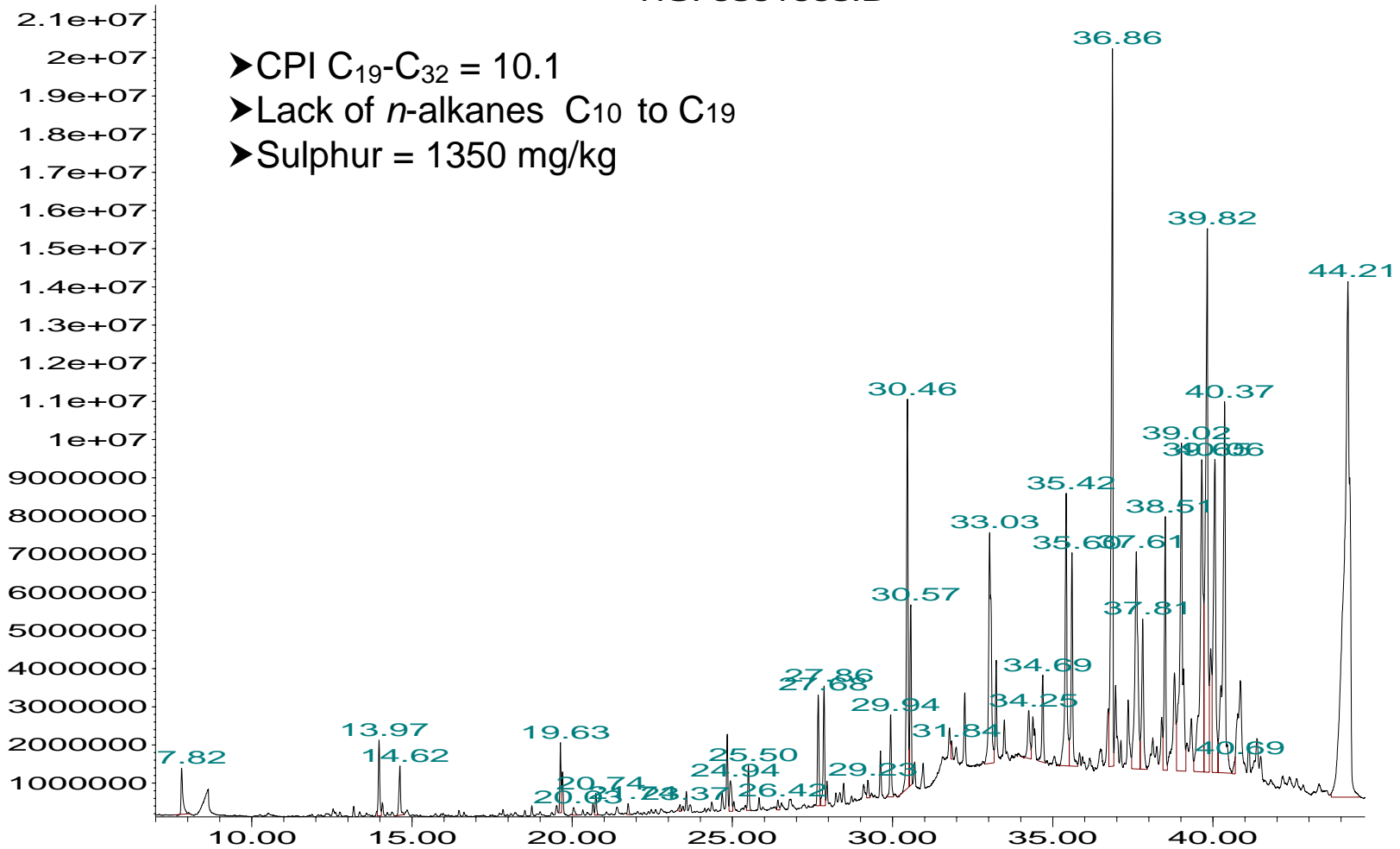


- CPI C₁₀-C₁₉ = 1.0
- CPI C₁₉-C₃₂ = 1.0
- Sulphur = 3380 mg/kg

GCMS Total Ion Chromatogram: Biogenic Sample

Abundance

TIC: 0501005.D



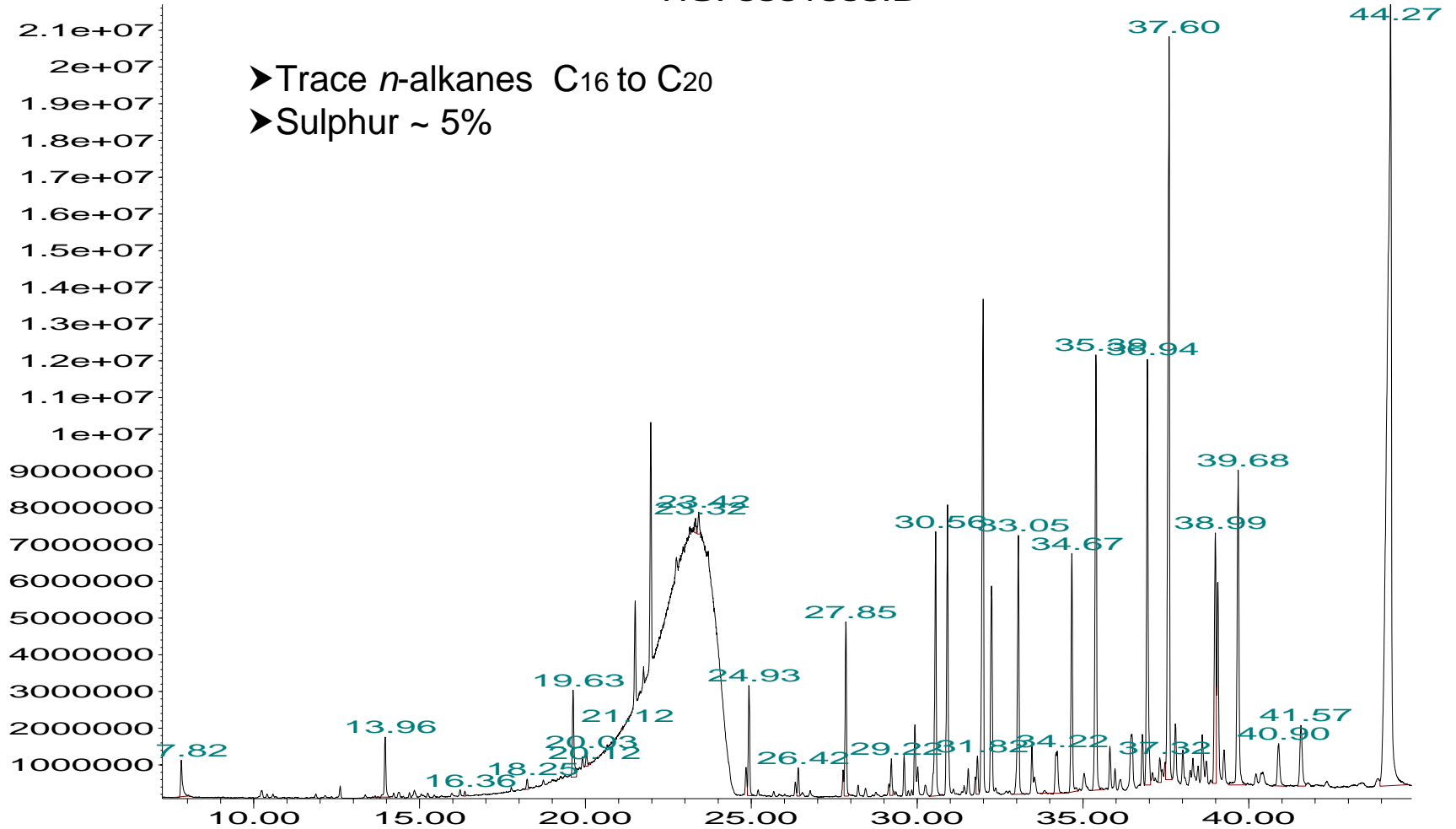
- ▶ CPI C₁₉-C₃₂ = 10.1
- ▶ Lack of *n*-alkanes C₁₀ to C₁₉
- ▶ Sulphur = 1350 mg/kg

Time-->

GCMS Total Ion Chromatogram: Biogenic-Petrogenic Mix

Abundance

TIC: 0901009.D

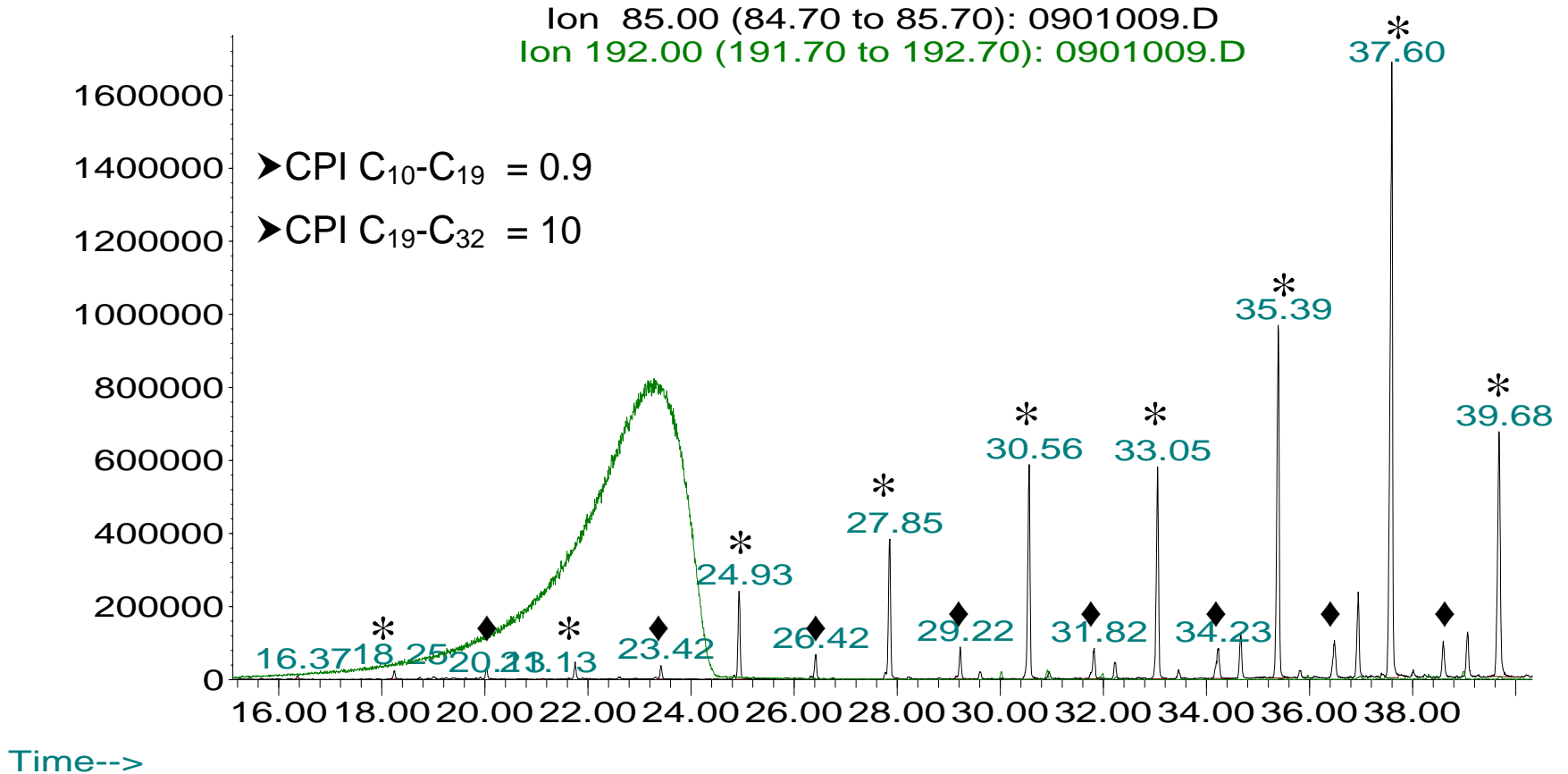


- ▶ Trace *n*-alkanes C₁₆ to C₂₀
- ▶ Sulphur ~ 5%

Time-->

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

Abundance

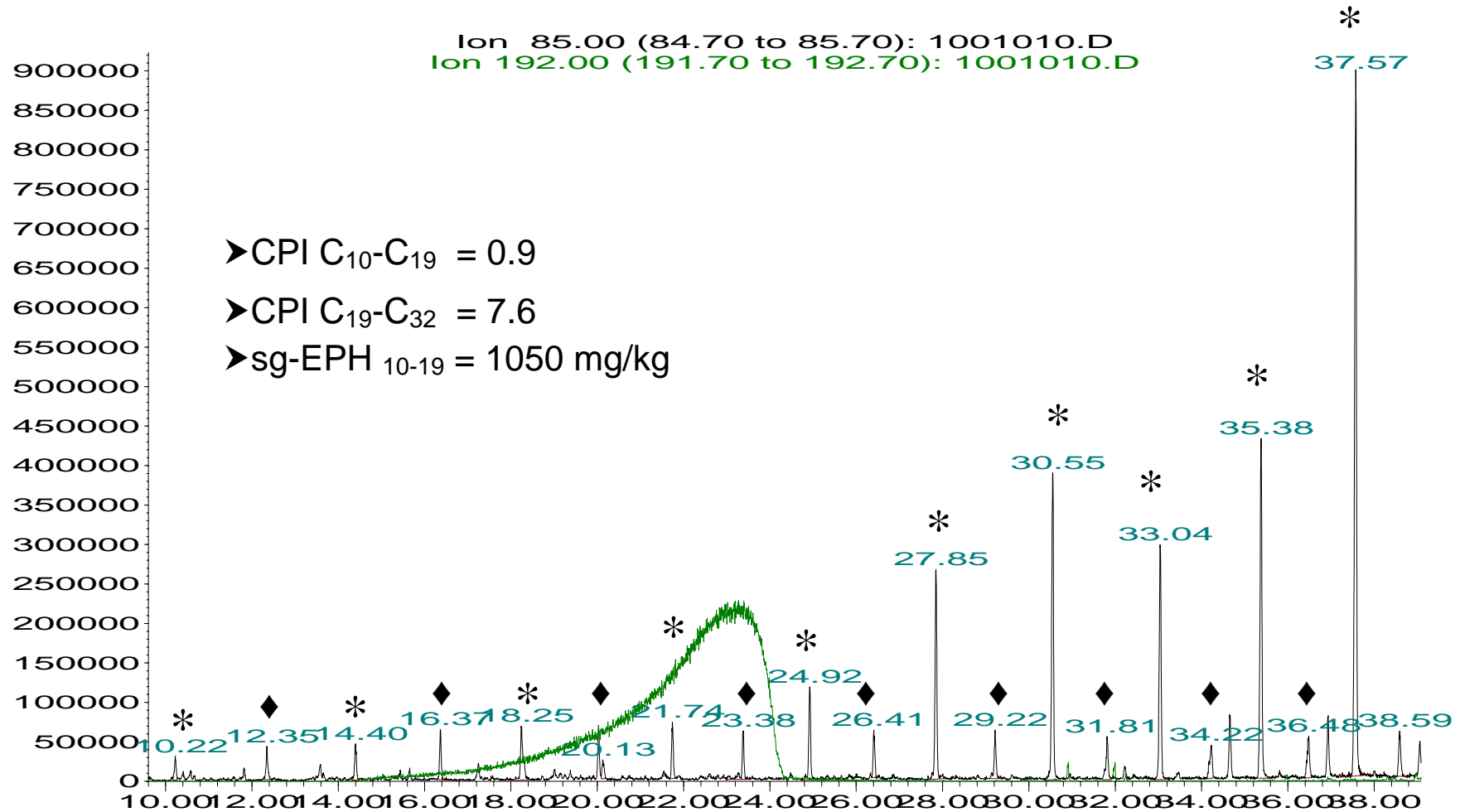


* = odd carbon # n-alkanes

◆ = even carbon # n-alkanes

Petrogenic-Biogenic Mix Second Example

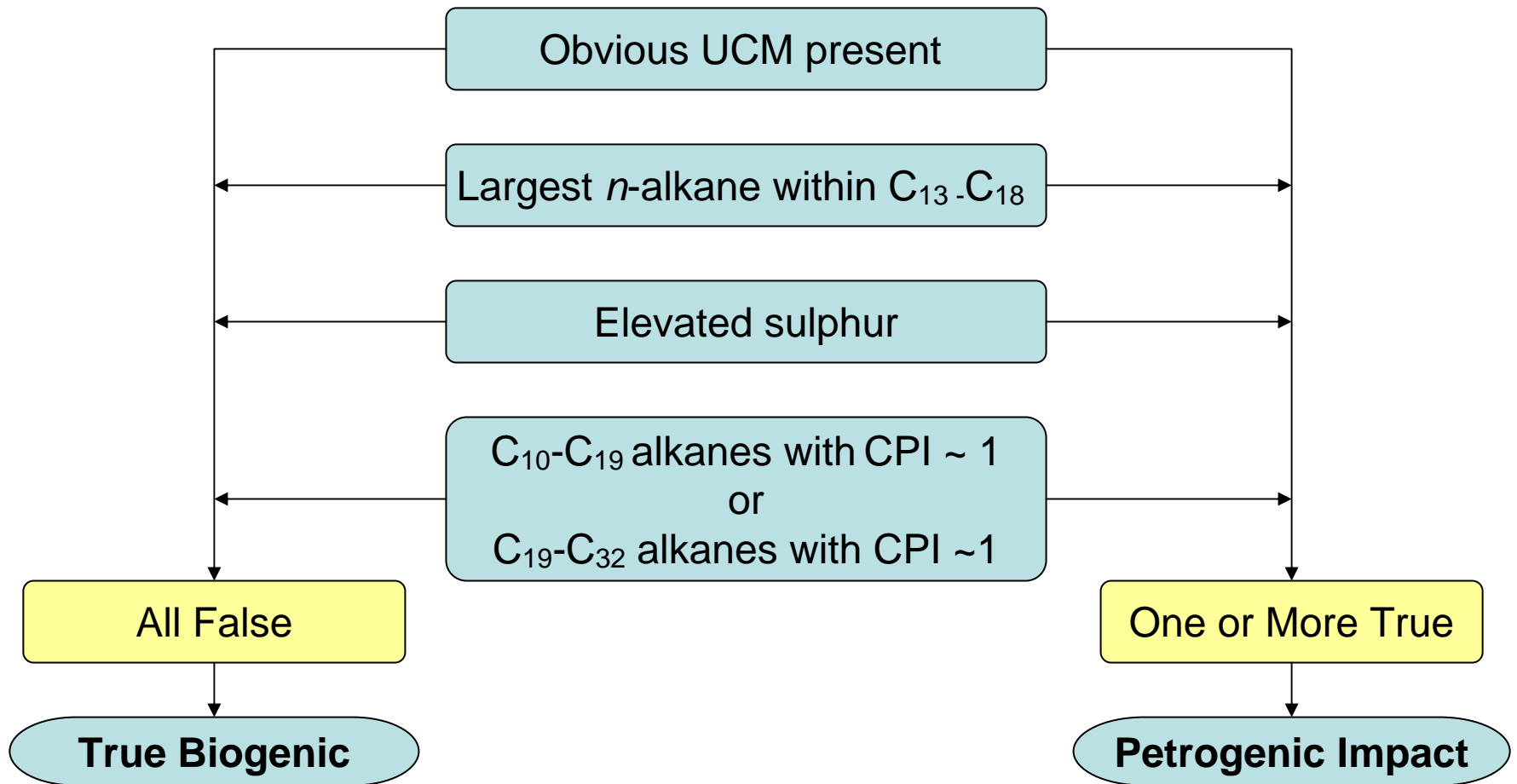
Abundance



* = 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 EPH₁₀₋₁₉ and EPH₁₉₋₃₂
- Total Sulphur

Determination of “*Contaminated Peat*”

- sg-EPH₁₀₋₁₉ compared to BC CSR uncorrected
 - **[1000 mg/kg]**
- sg-EPH₁₉₋₃₂ 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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