Insight into the Composition and Structure of Petroleum Metabolites Not Identified by Standard Methods of Analysis

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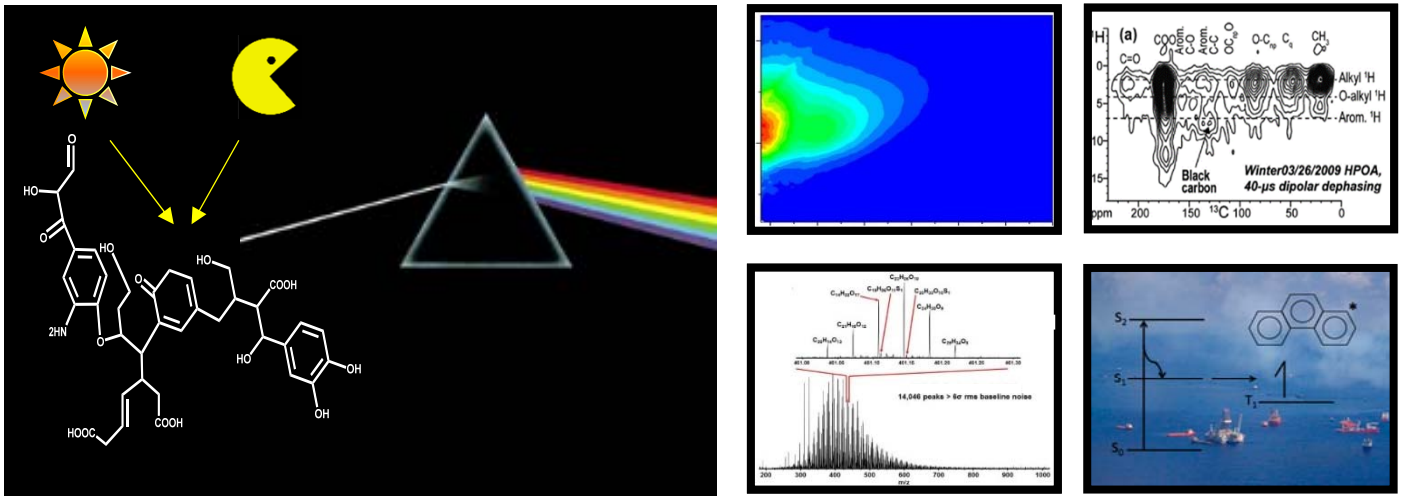
Battelle – 2018 Chlorinated Conference

Palm Springs, California

April 12, 2018

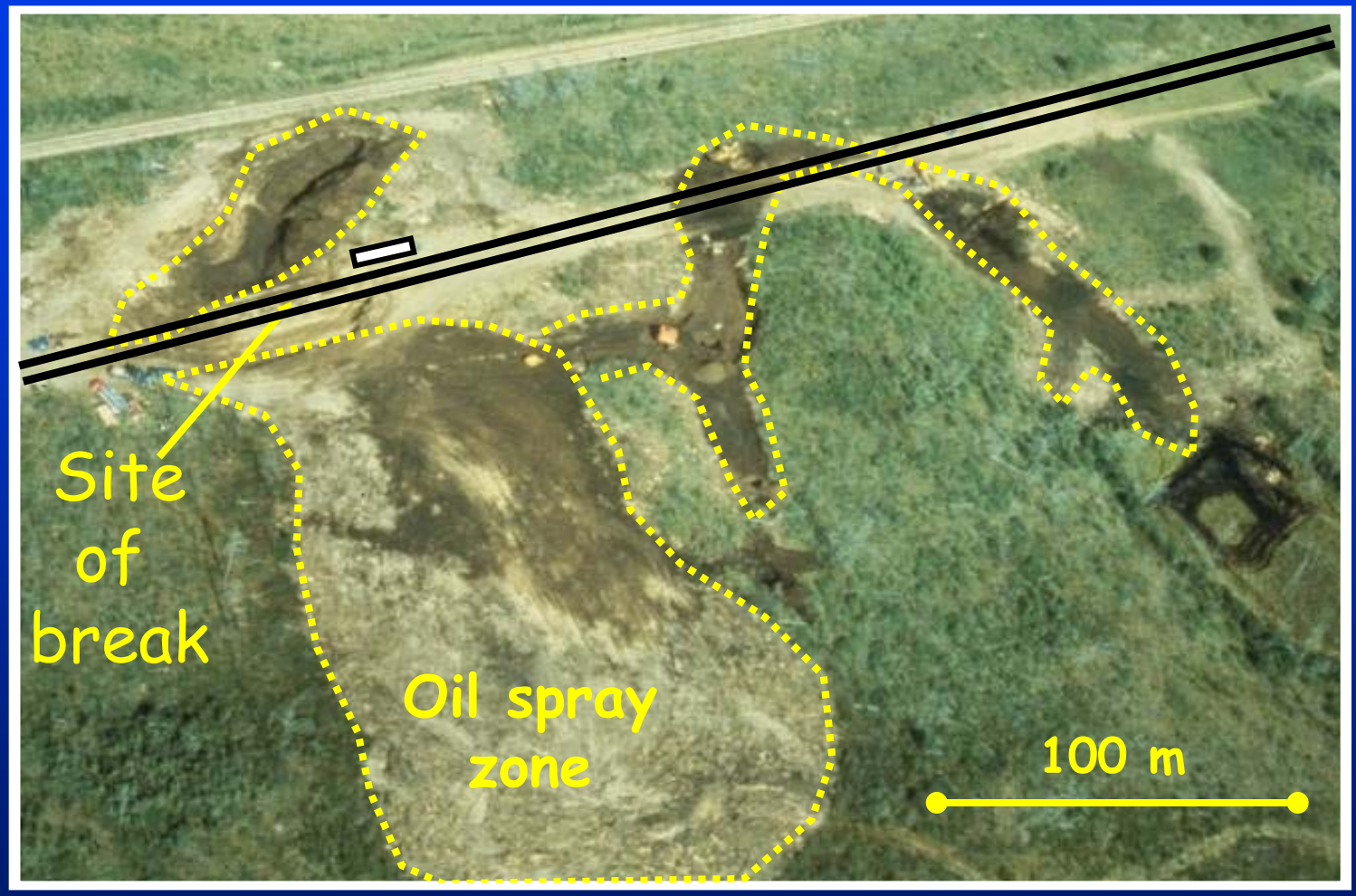


Considerations

- Natural organic matter (NOM) is continuous in molecular-level composition and structure
  - Size
  - Shape
  - Heteroatom D
  - Aromaticity
  - Etc.

- The molecular and structure of dissolved o is always similar to the parent organic matter source

National Crude Oil Spill Fate and Natural Attenuation Research Site

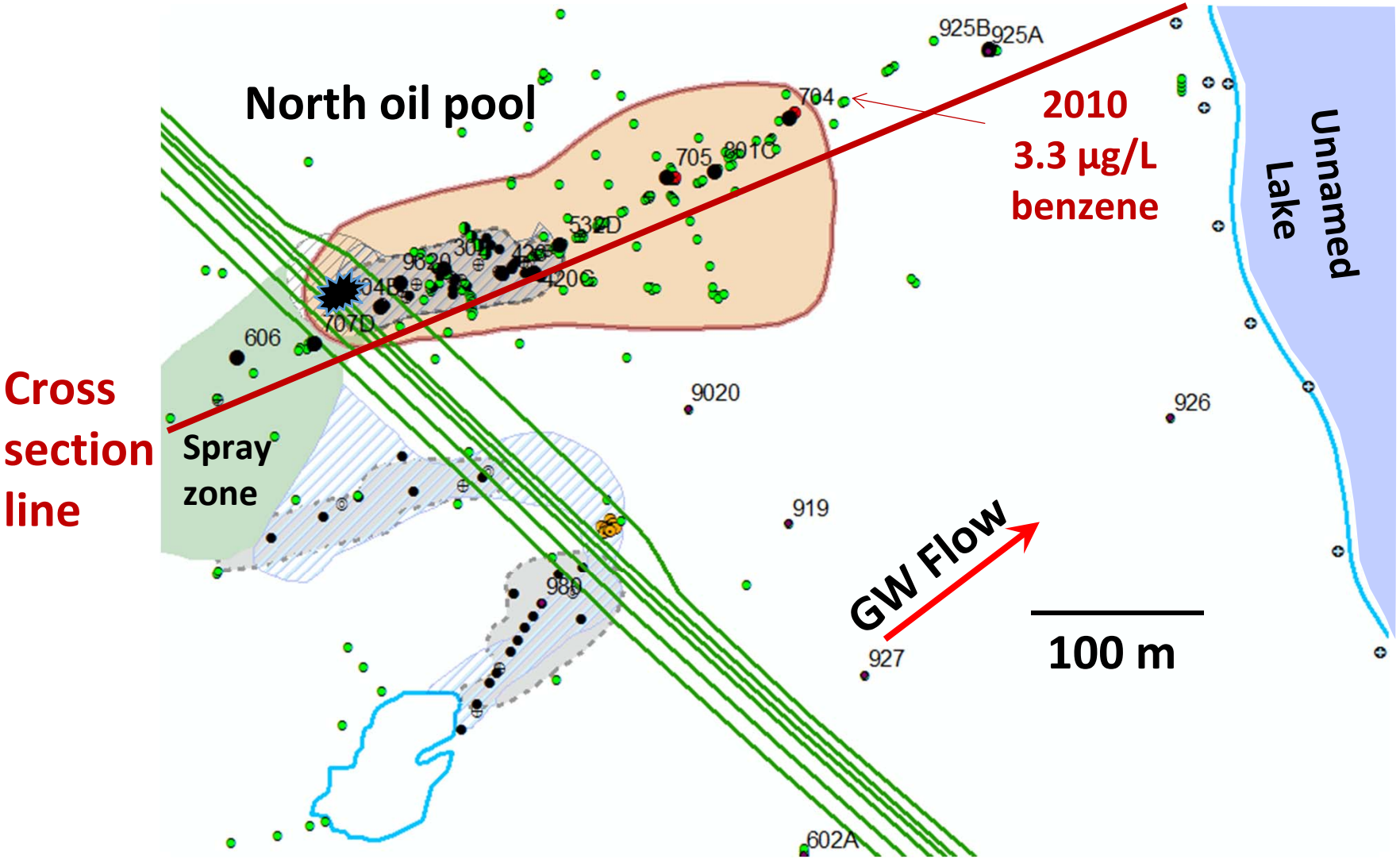


August, 1979

USGS

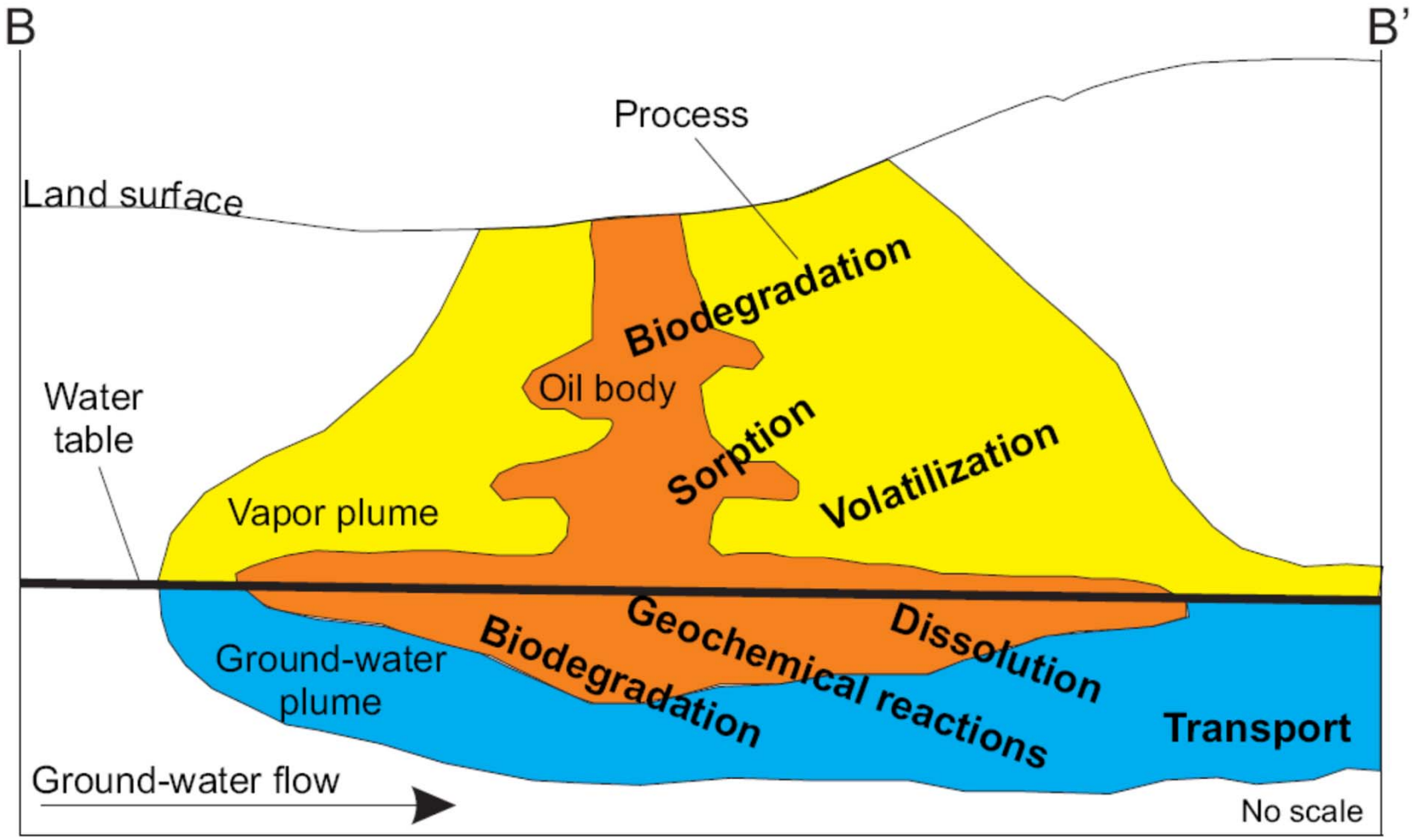
Courtesy of Barbara A. Bekins

North Oil Pool and Plume



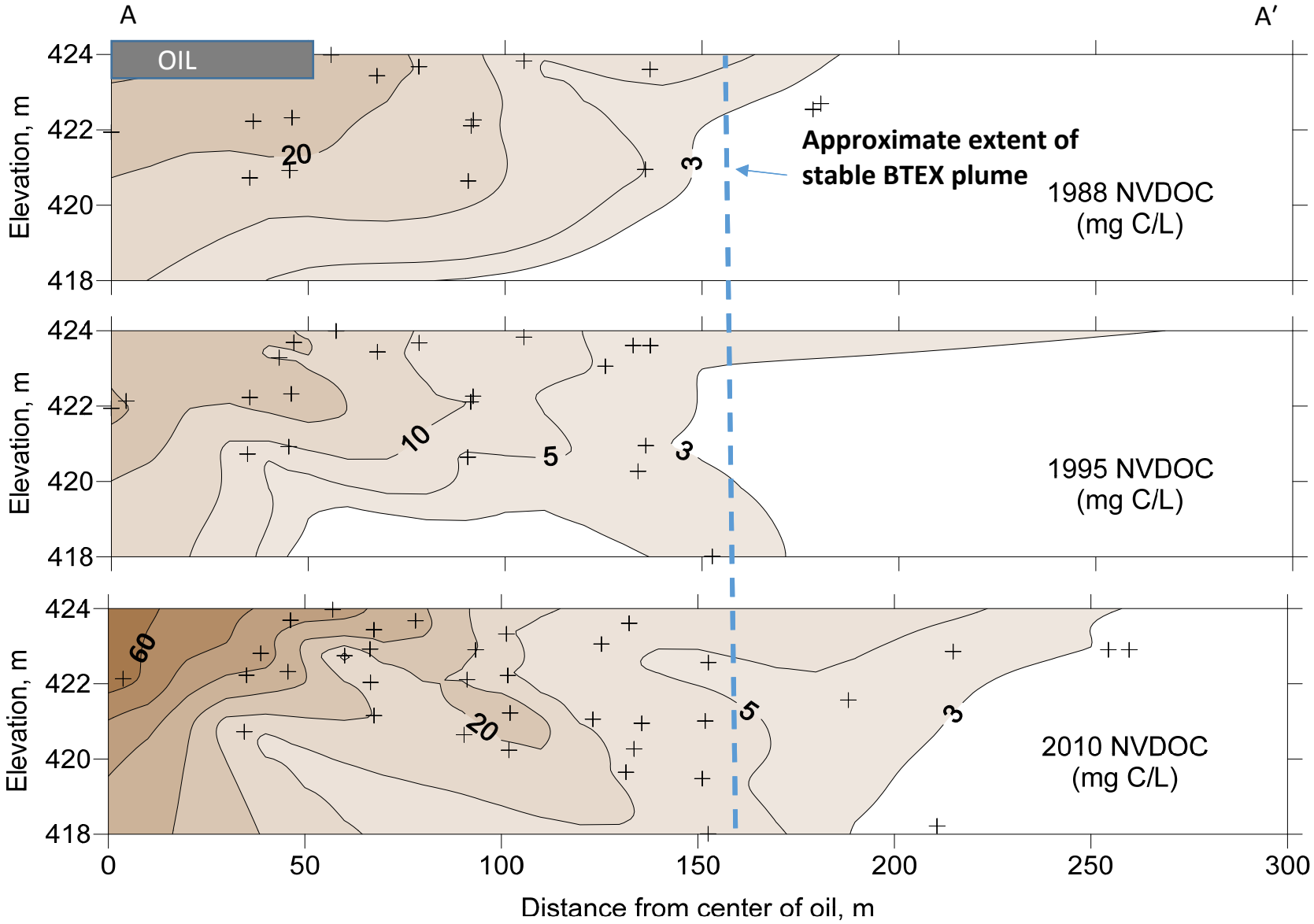
Courtesy of Barbara A. Bekins

Biologically-Derived Dissolved Organic Matter from Petroleum (DOM_{HC})



Courtesy of Barbara A. Bekins

The DOM_{HC} Plume at the Bemidji Site is Expanding

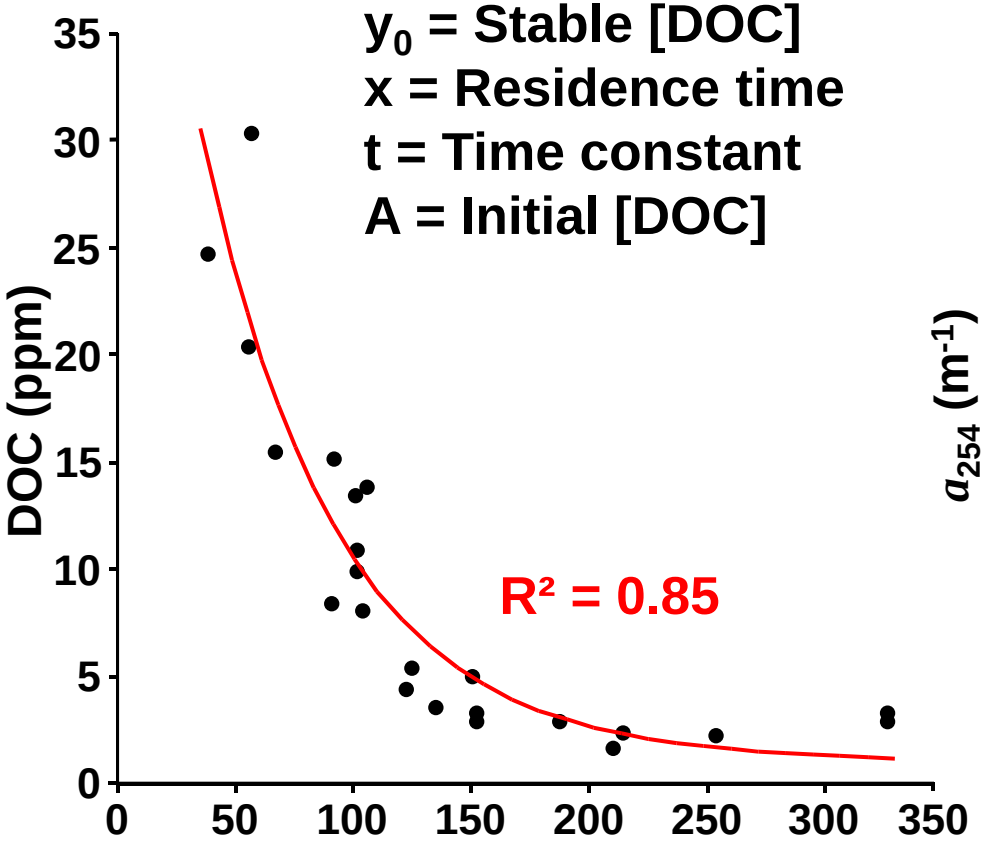


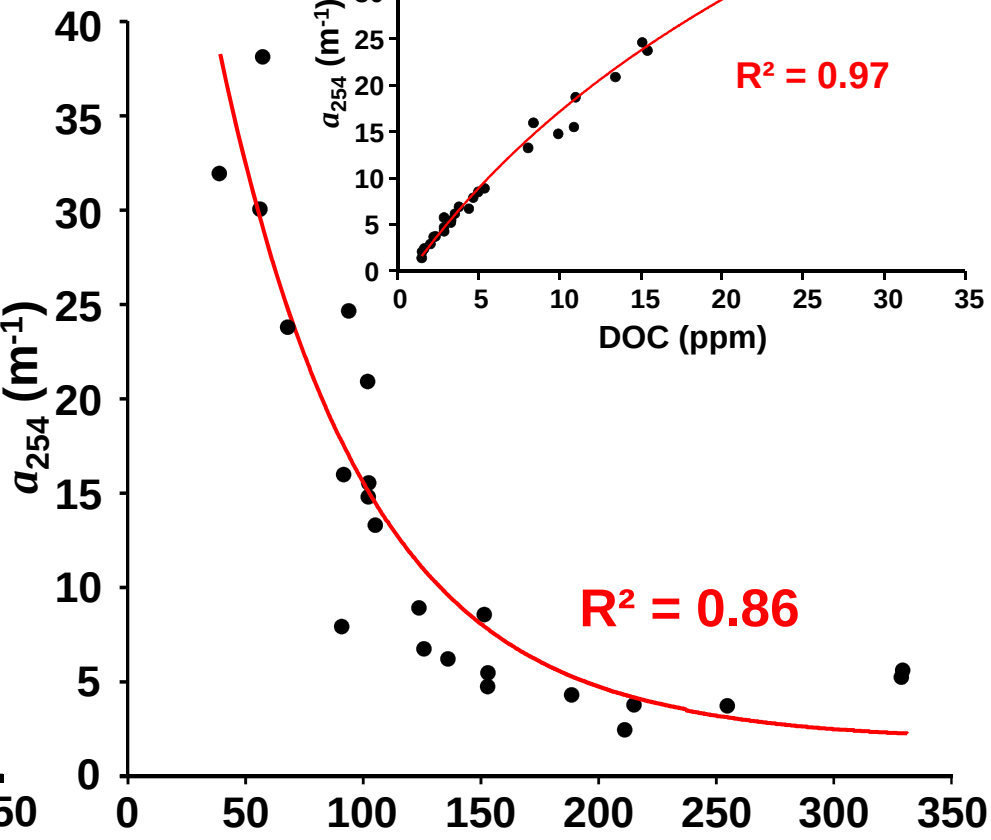
Bekins et al., 2016

Natural Attenuation of Petroleum-Derived DOM by Optical Spectroscopy

$$y = y_0 + Ae^{x/t}$$

y = Modeled [DOC] at t
y_0 = Stable [DOC]
x = Residence time
t = Time constant
A = Initial [DOC]

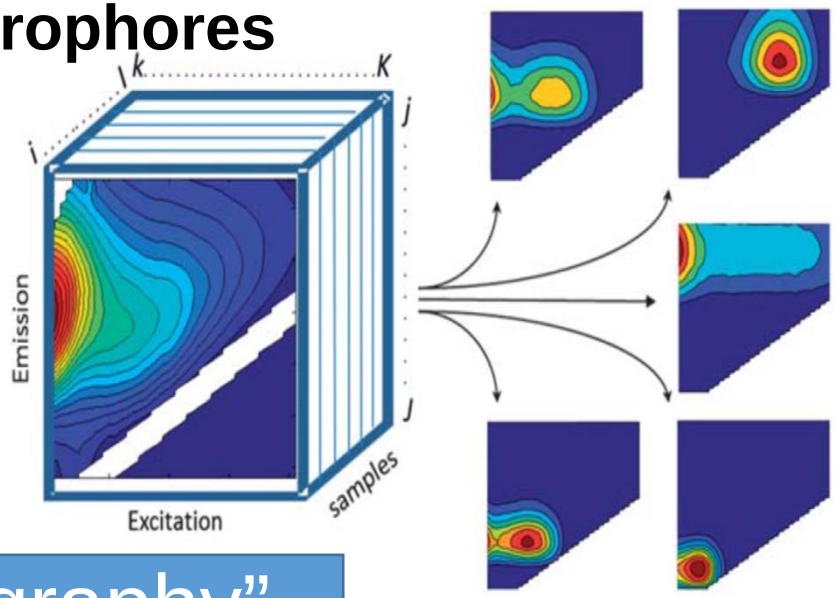




Distance from Center of Oil (m)

Parallel Factor (PARAFAC) Analysis of Excitation Emission Matrix (EEM) Spectra

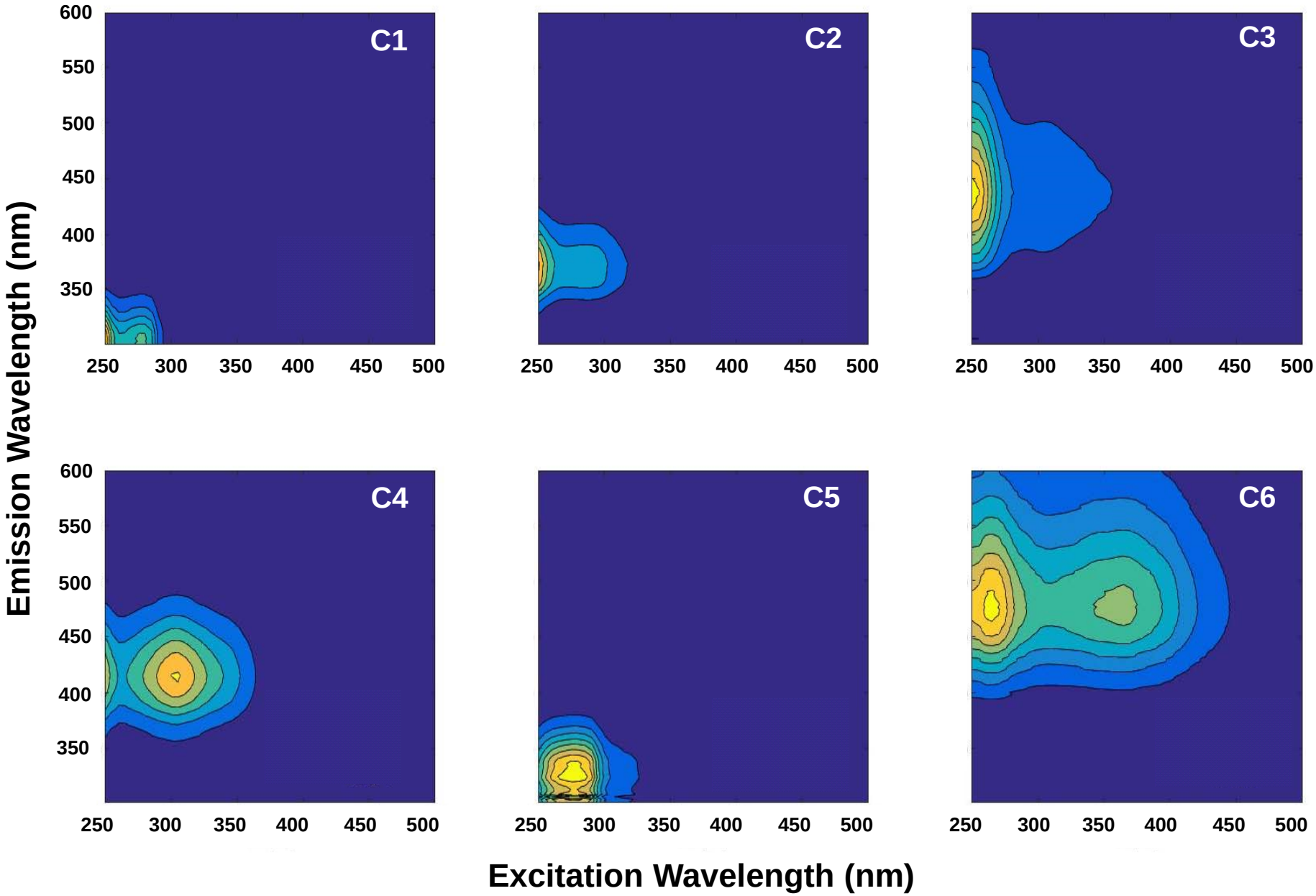
- **Decomposes EEMs underlying chemical components**
  - **Represents the values of fluorophores to each component**
  - **Leads to mathematical identification and quantification of varying fluorophores**
- **Environmental samples**
  - **Composition?**
  - **Identity of fluorophores?**



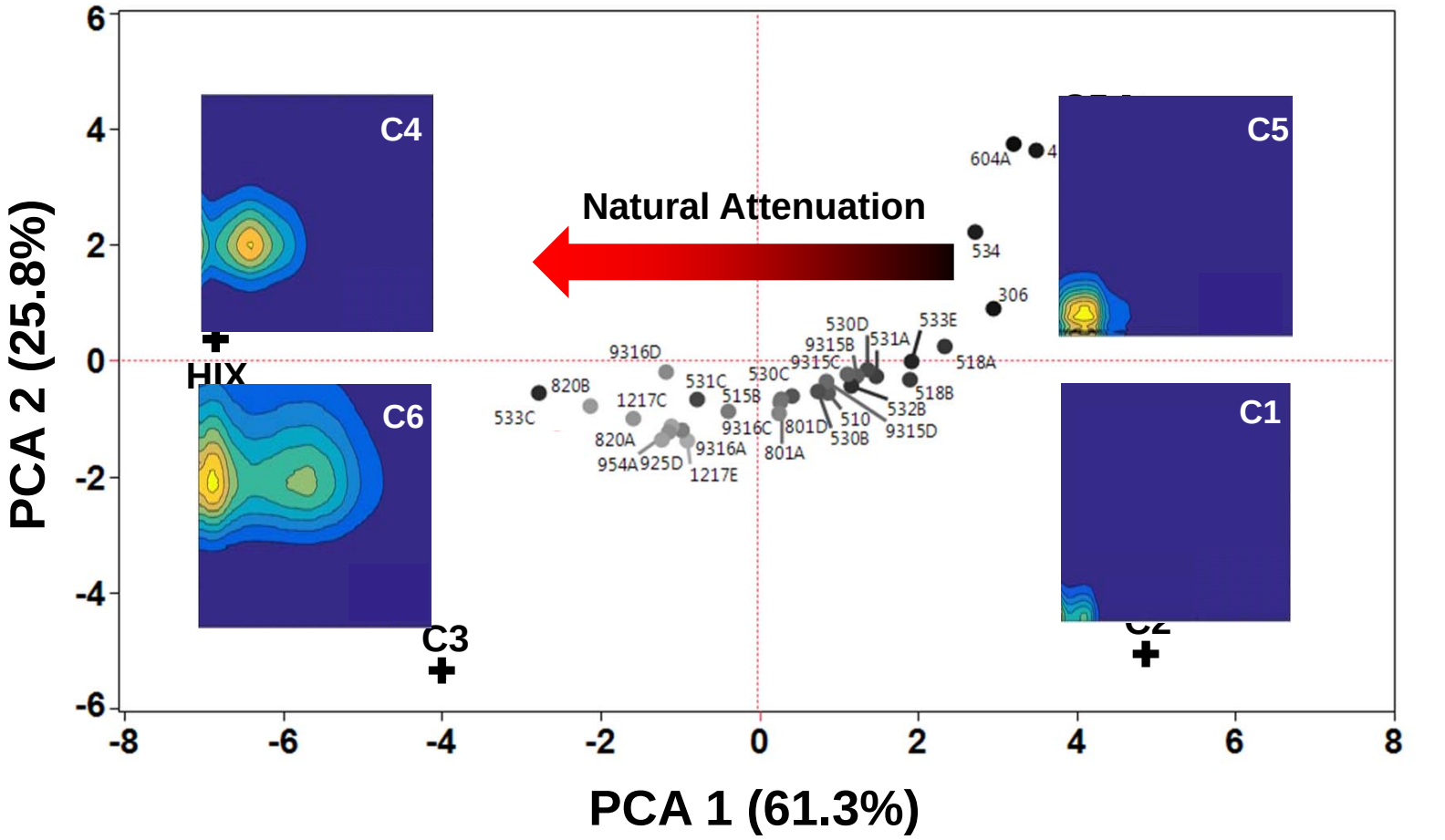
"Mathematical Chromatography"

Stedmon and Wünsch <urbw@aqua.dtu.dk>

PARAFAC Components – Petroleum-Derived DOM



Natural Attenuation of DOM_{HC} by Optical Spectroscopy

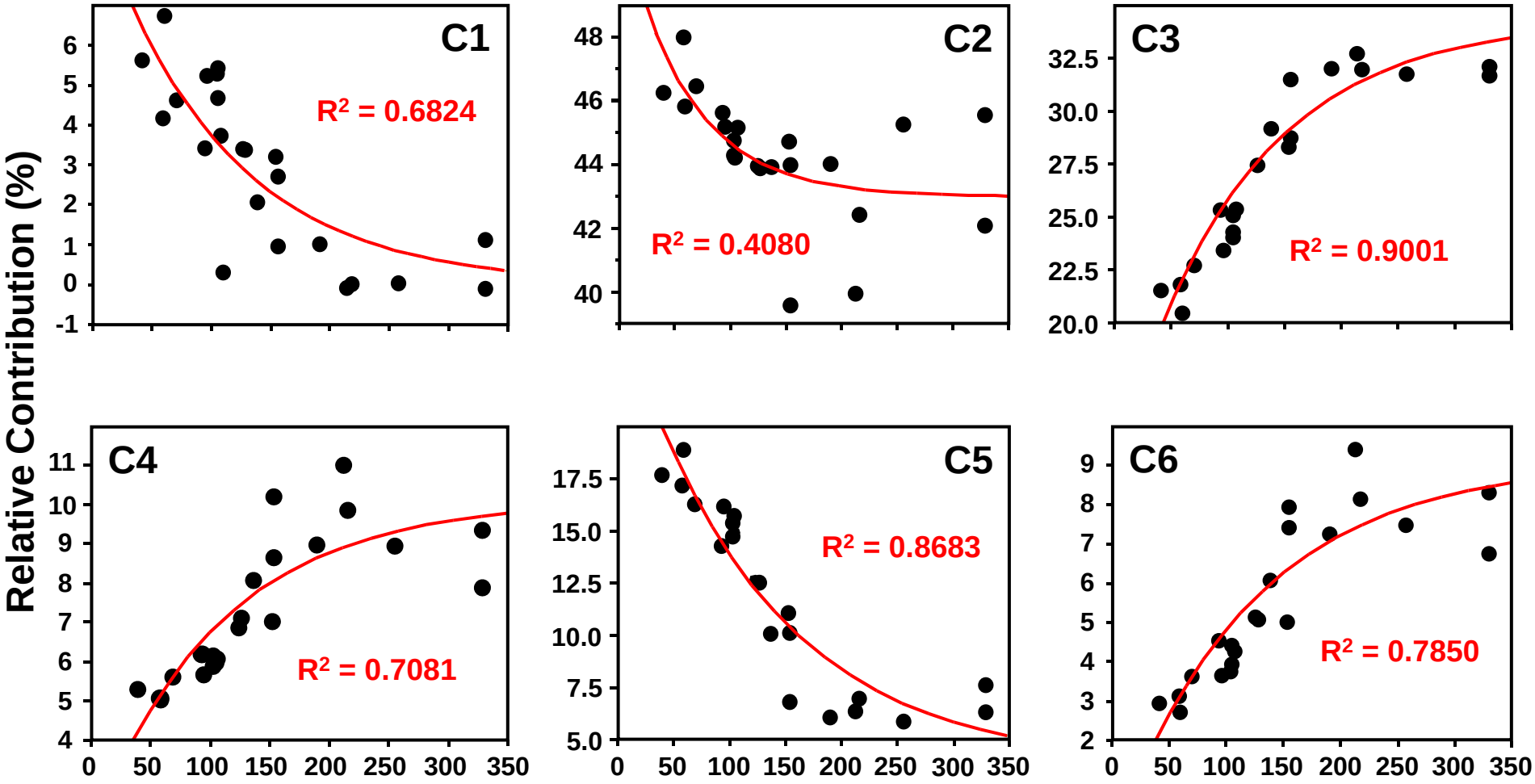


● Native Groundwater DOM

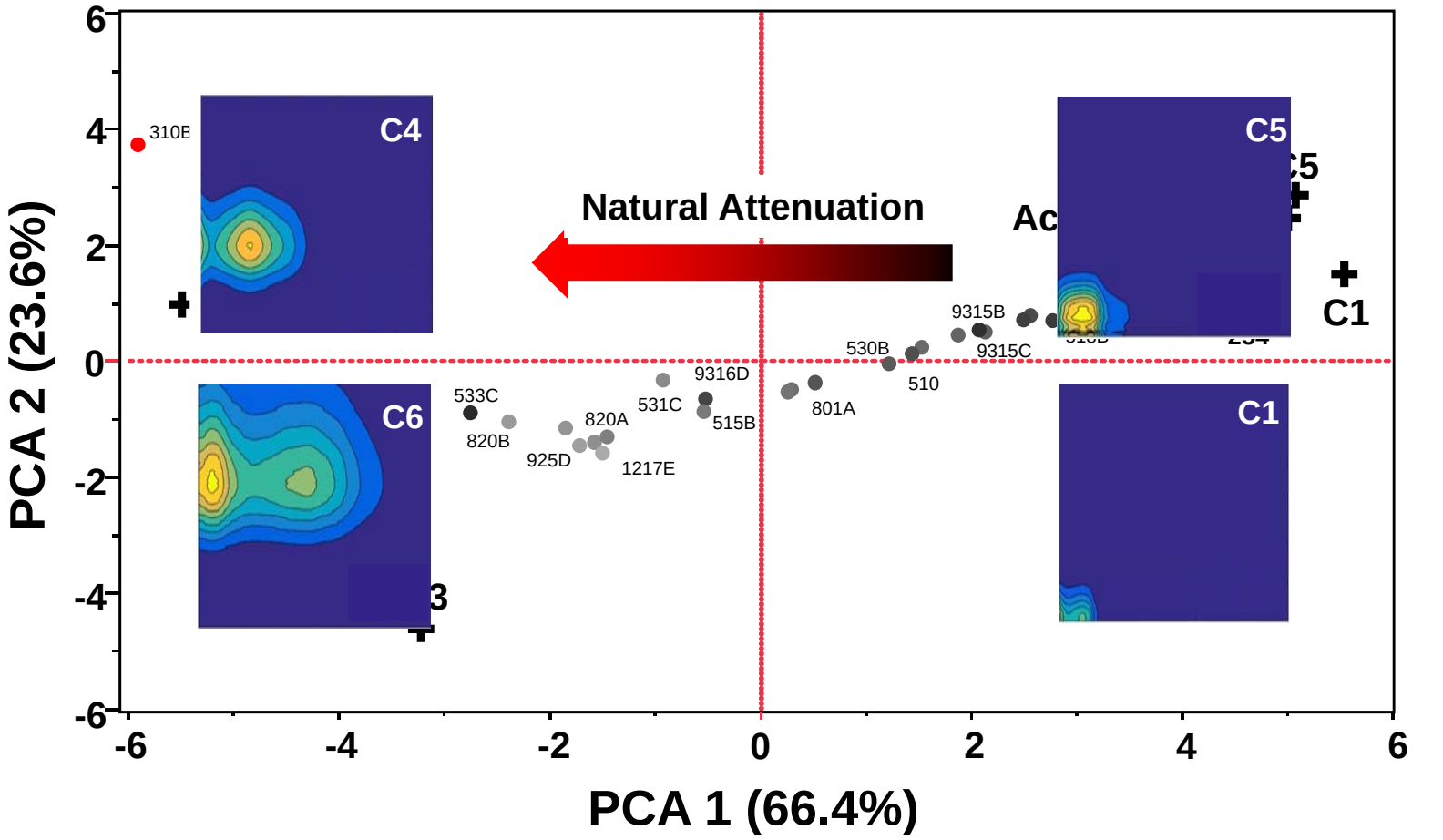
Distance from Source

HIX = Humification Index
C1-C6 = PARAFAC Components 1-6
a_{254} = Absorbance at 254 nm

$CDOM_{HC}$ Continuum by EEMS



PARAFAC Components and Toxicity?



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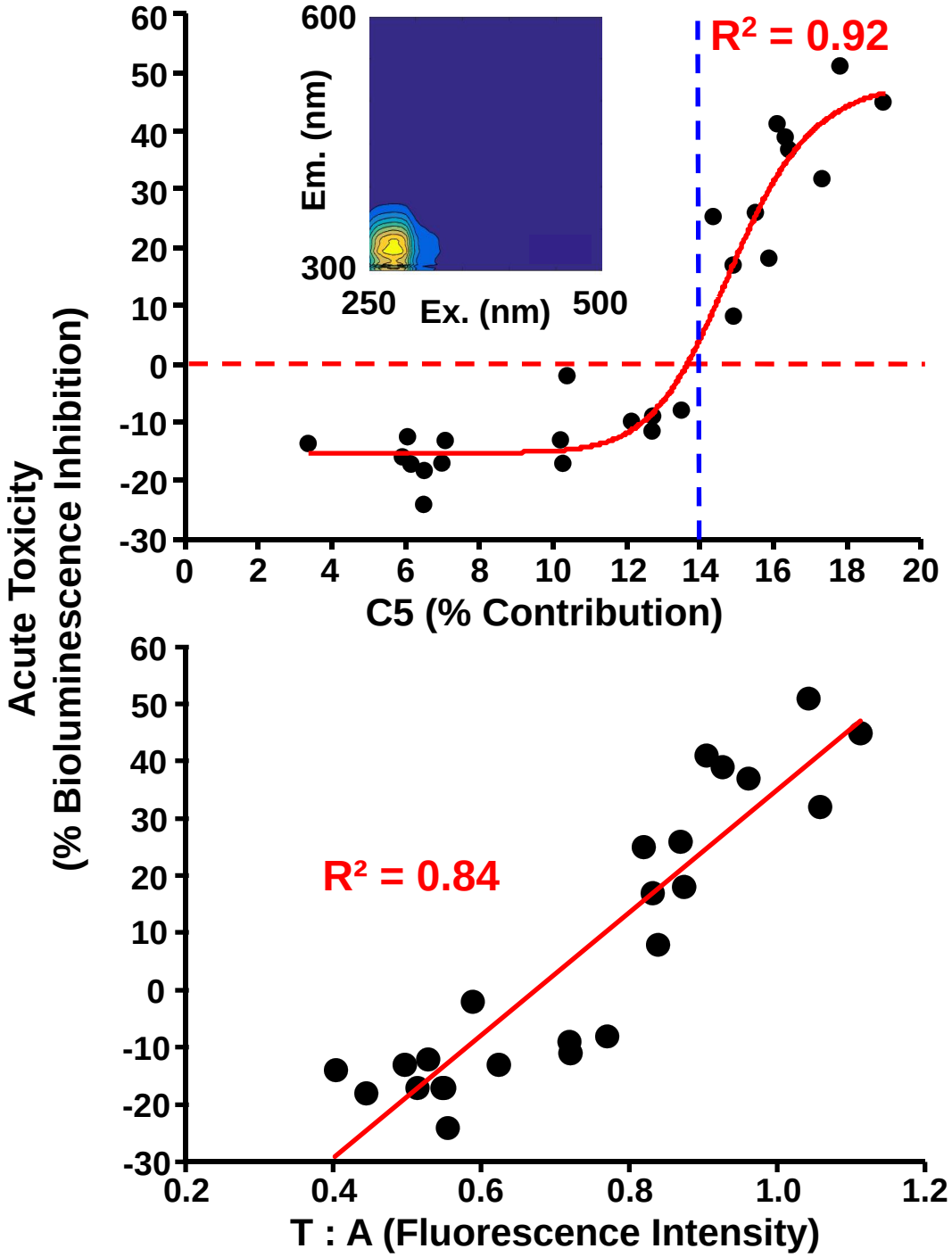
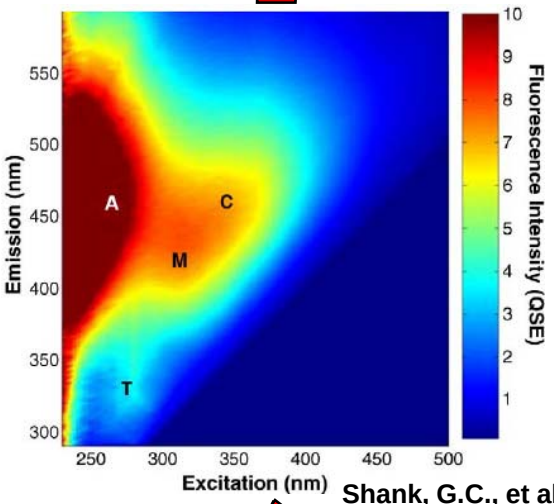
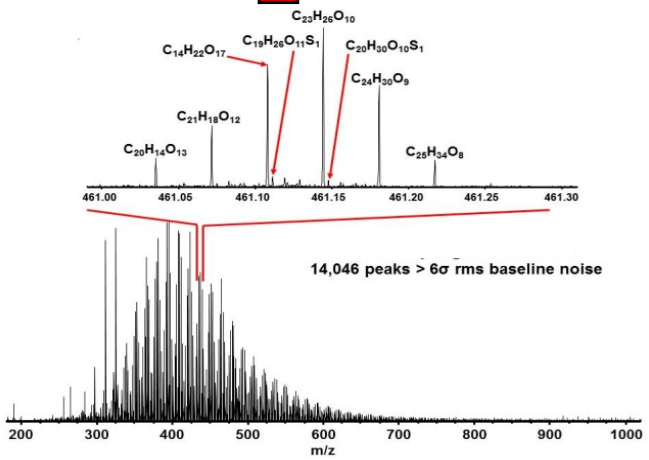

Acute Toxicity
(% Bioluminescence Inhibition)
C5 (% Contribution)
R² = 0.92
Em. (nm)
Ex. (nm)
600
300
250
500
T : A (Fluorescence Intensity)
R² = 0.84

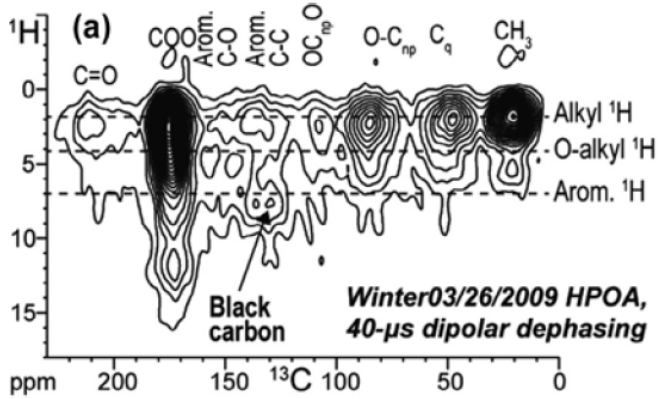
Molecular-Level Composition and Structure by Optical Spectrocopy?

High Throughput: Optical Properties and Molecular-Level Composition



Shank, G.C., et al. 2010

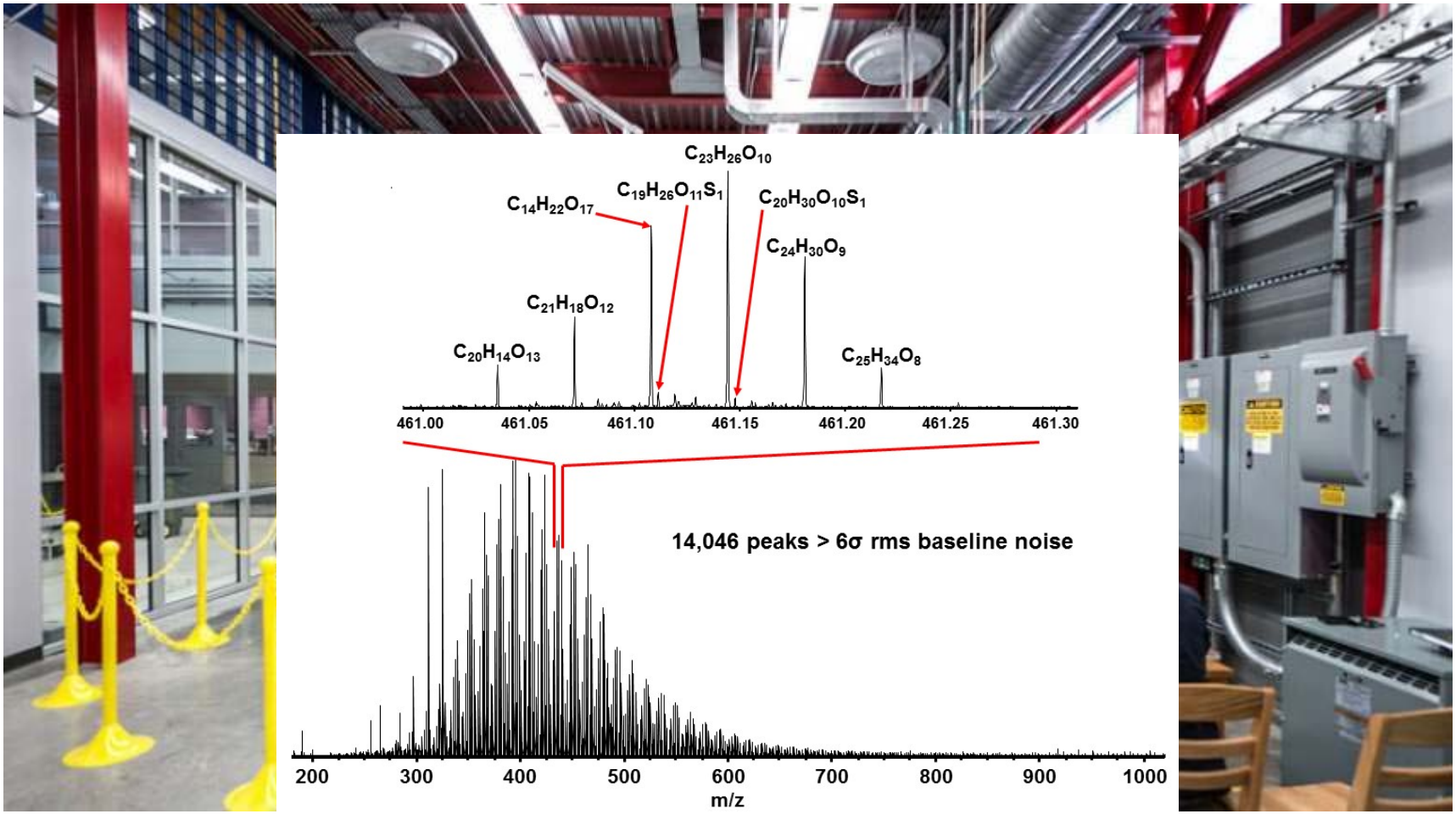




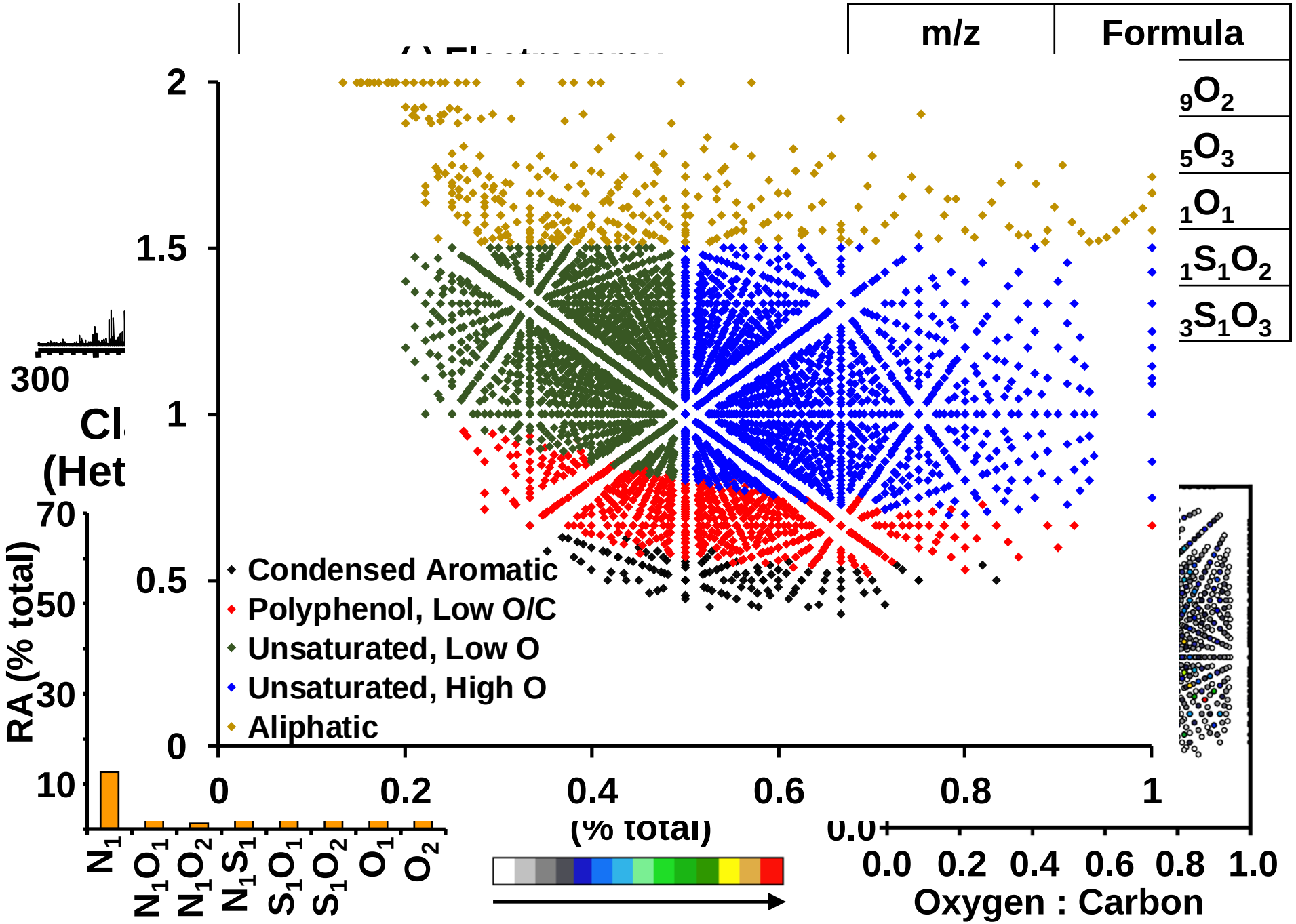
Cao, et al. 2016

Molecular-Level Composition and Structure

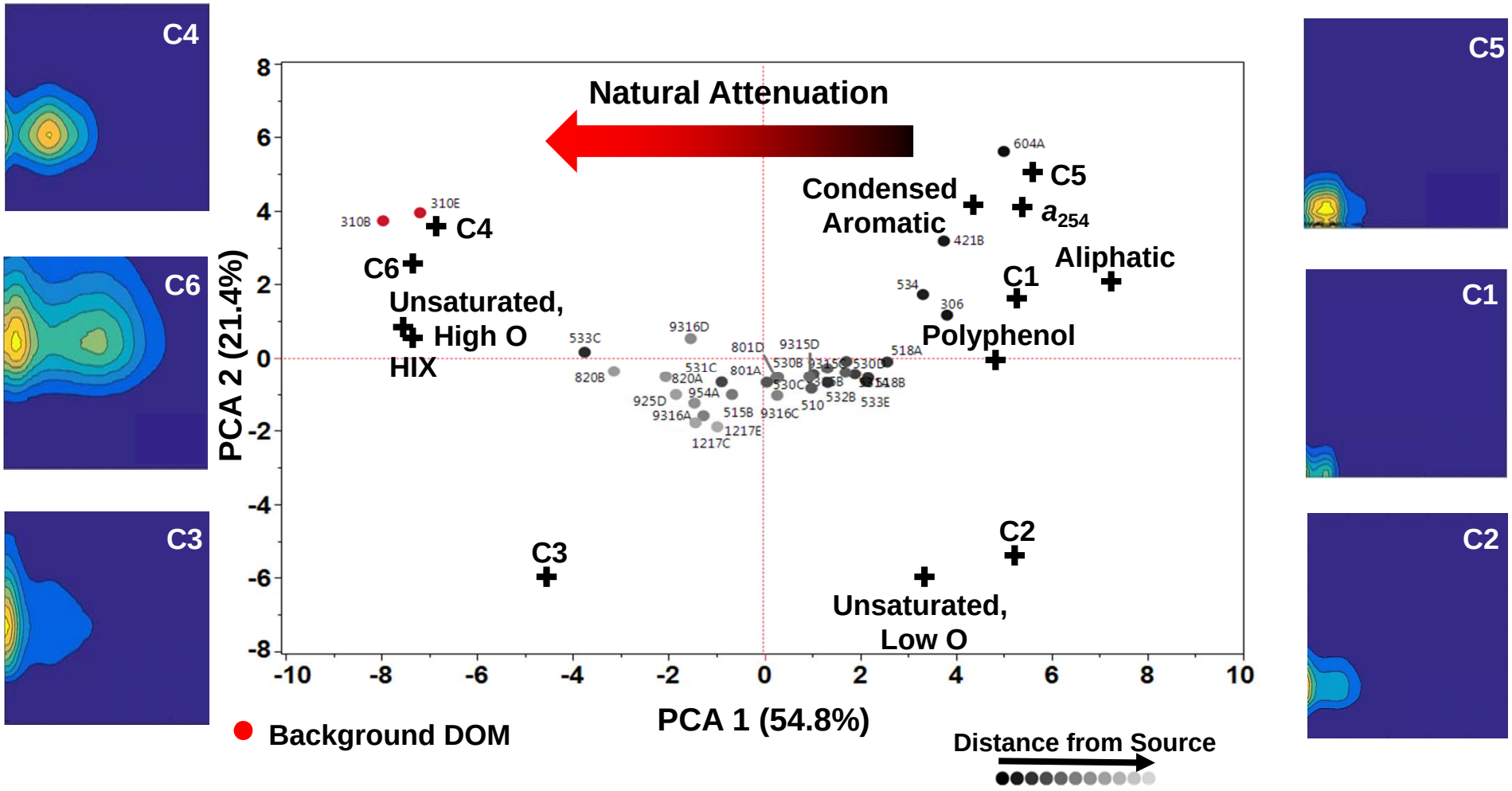
Ultrahigh Resolution Mass Spectrometry



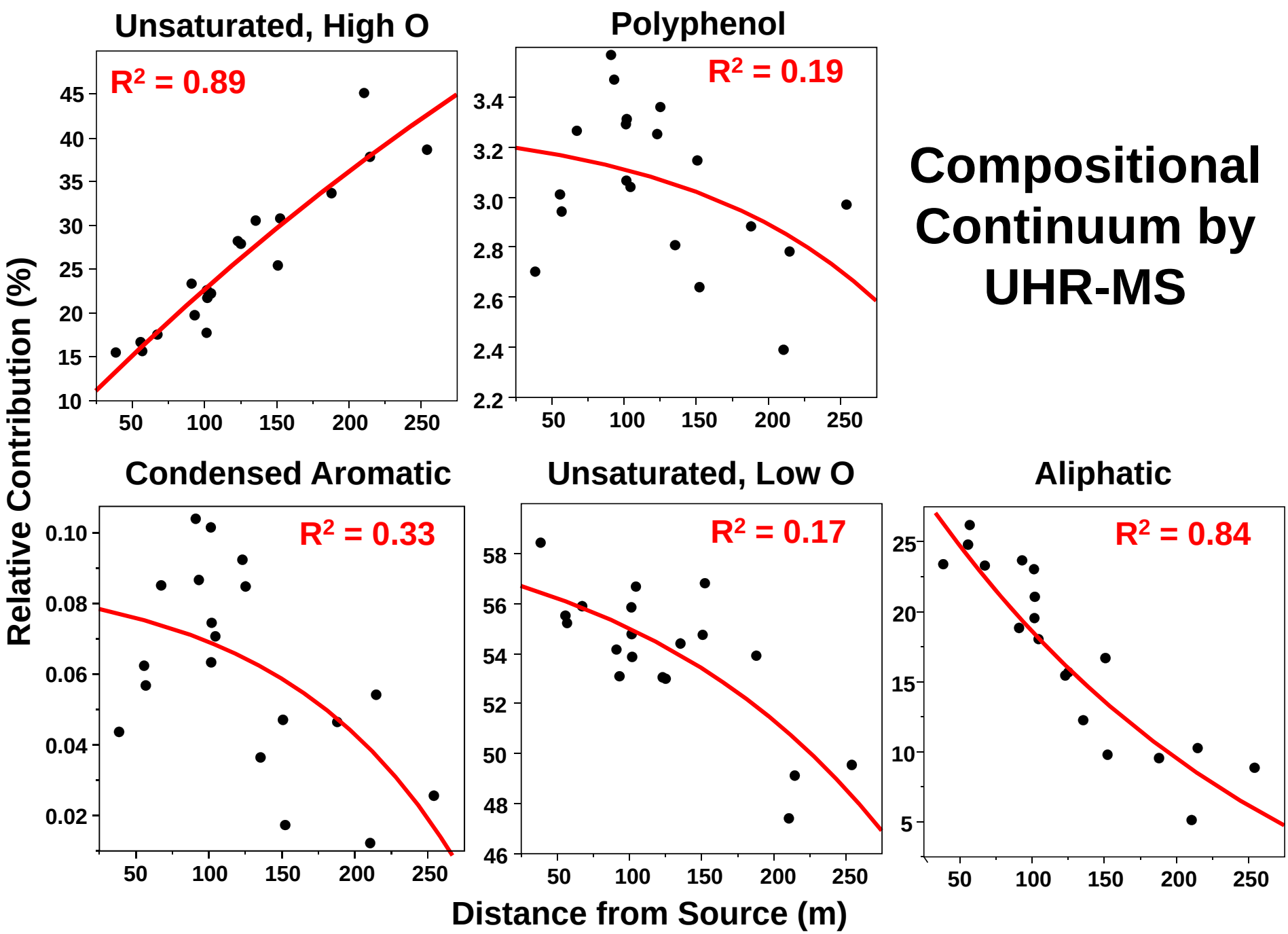
Compositional Information from FT-ICR MS



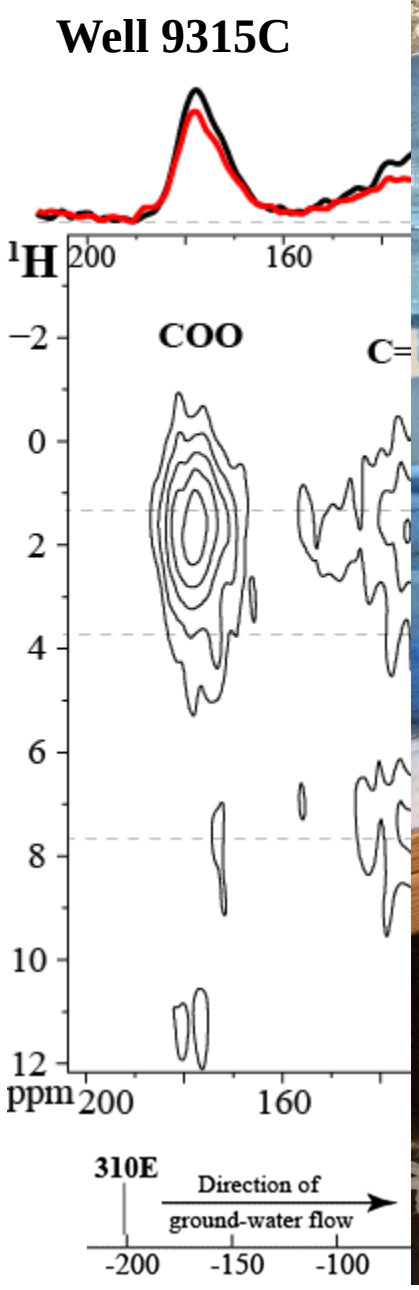
Natural Attenuation of DOM_{HC} at the Molecular Level by Optical Spectroscopy and UHR-MS



HIX = Humification Index
C1-C6 = PARAFAC Components 1-6
a_{254} = Absorbance at 254 nm


Unsaturated, High O
R² = 0.89
Polyphenol
R² = 0.19
Compositional Continuum by UHR-MS
Condensed Aromatic
R² = 0.33
Unsaturated, Low O
R² = 0.17
Aliphatic
R² = 0.84
Relative Contribution (%)
Distance from Source (m)

Stru ¹H)

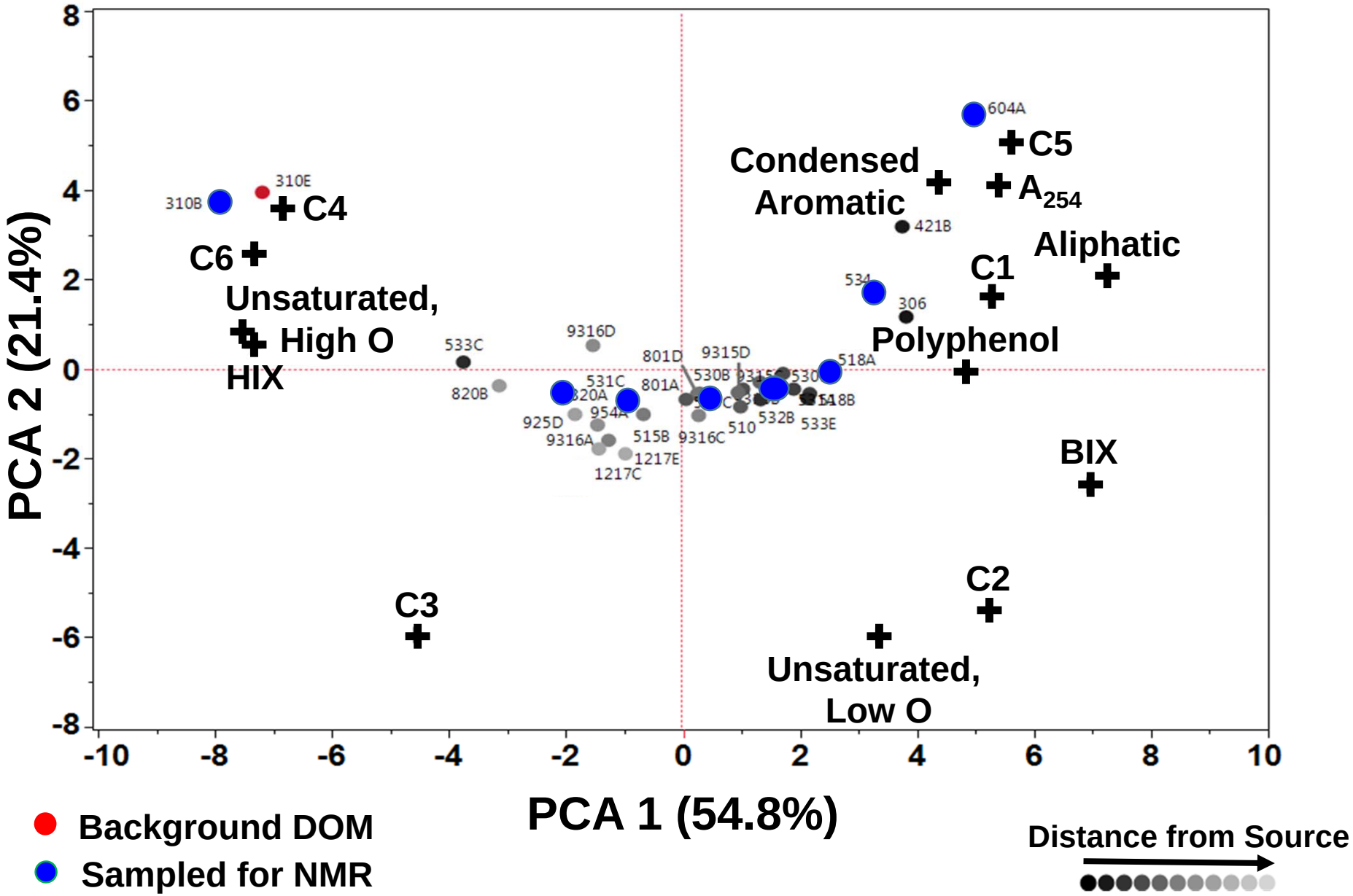


atic OC carbons
ear alkyl
onents, not in
hydrates.

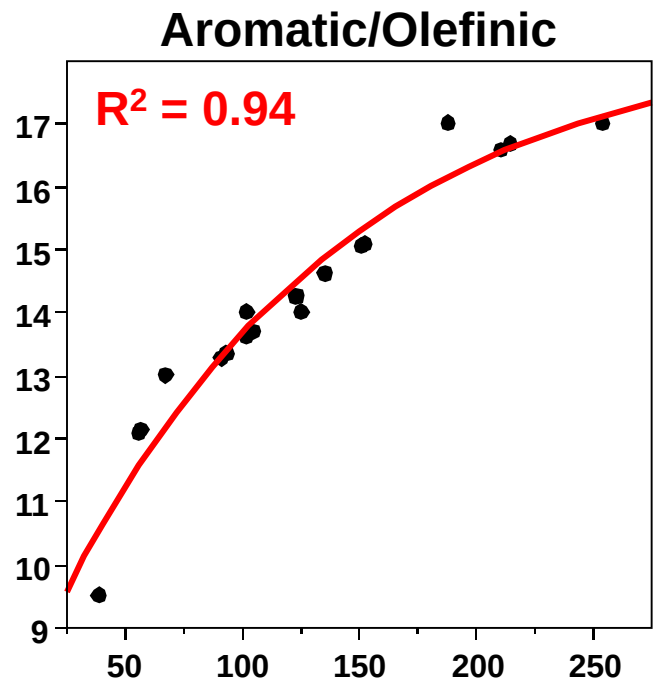
near alkyl
onent.

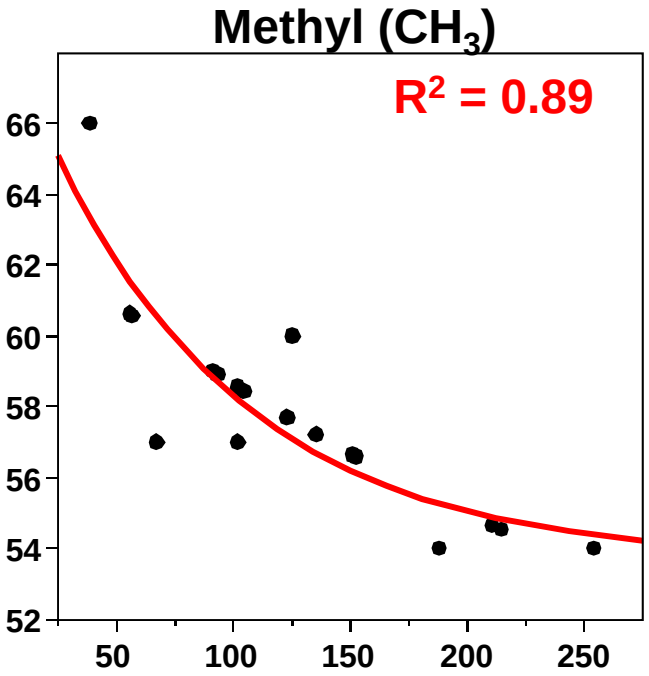
oxyl groups are
y attached to
carbons:
xylated aliphatic
clic?) molecules.

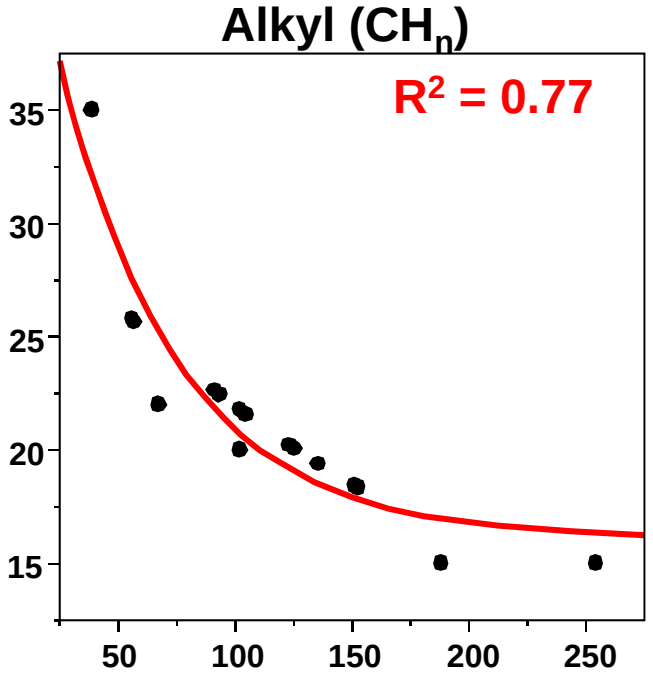
Structural Continuum by NMR Spectroscopy



Structural Continuum by NMR Spectroscopy

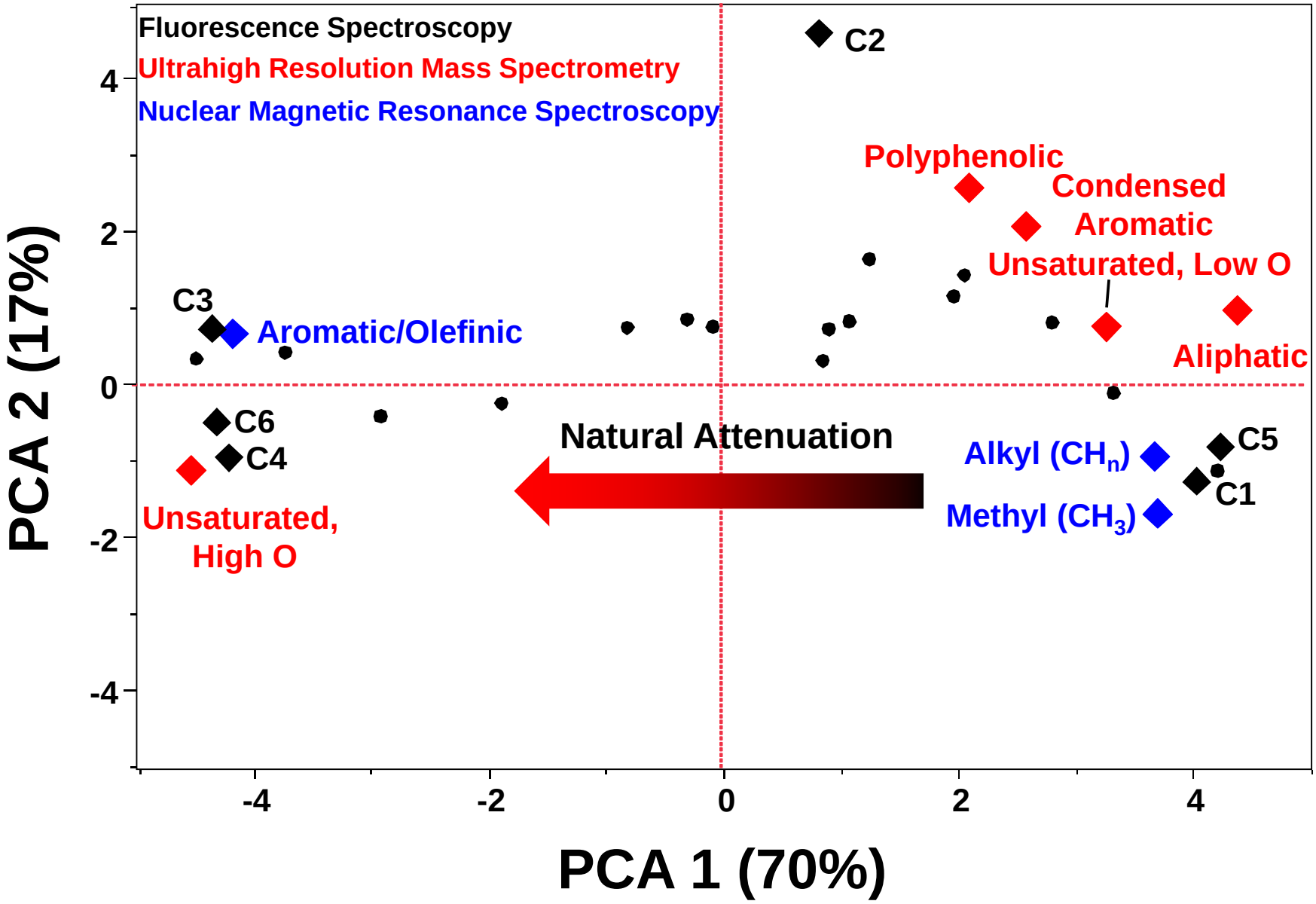






Distance from Center of Oil (m)

Relationship between Molecular Level Composition, Structure and Optical Properties of DOM_{HC}



Acknowledgements

- Jeanne Jaeschke
- Jared Trost
- Andrew Berg
- Bemidji Field Team

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Questions?