

# Characterization of Dissolved Organic Matter:

## Major advances by combining reversed-phase liquid chromatography and FT-ICR-MS

Boris P. Koch<sup>1,2</sup>

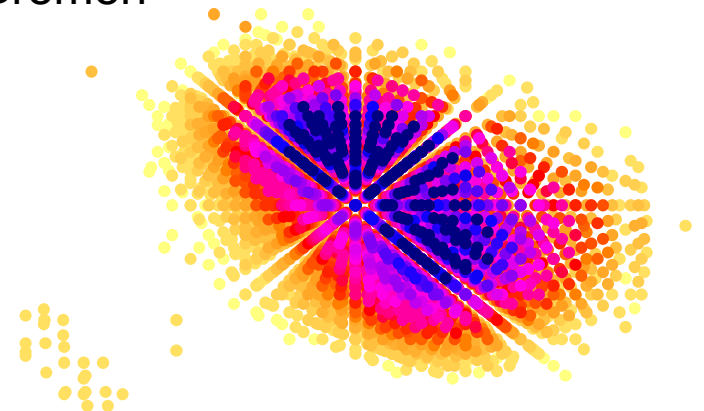
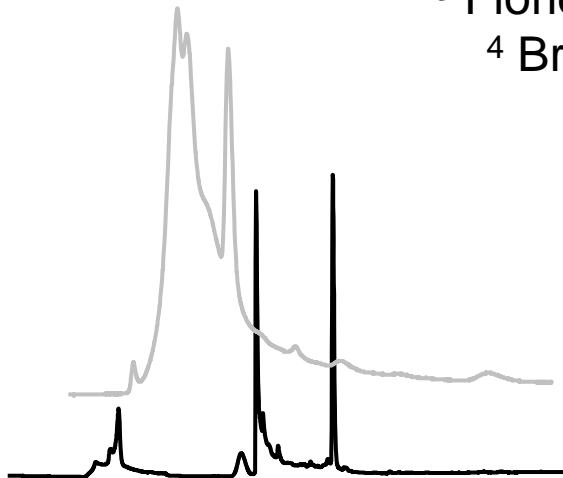
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<sup>1</sup> Alfred-Wegener-Institute for Polar and Marine Research, Bremerhaven

<sup>2</sup> University of Applied Science, Bremerhaven

<sup>3</sup> Florida State University, Tallahassee

<sup>4</sup> Bruker Daltonik GmbH, Bremen



# Outline

## Introduction

*FT-ICR-MS*

*Chromatography*

## Results

*Polarity-based*

*chromatography of DOM*

## Applications

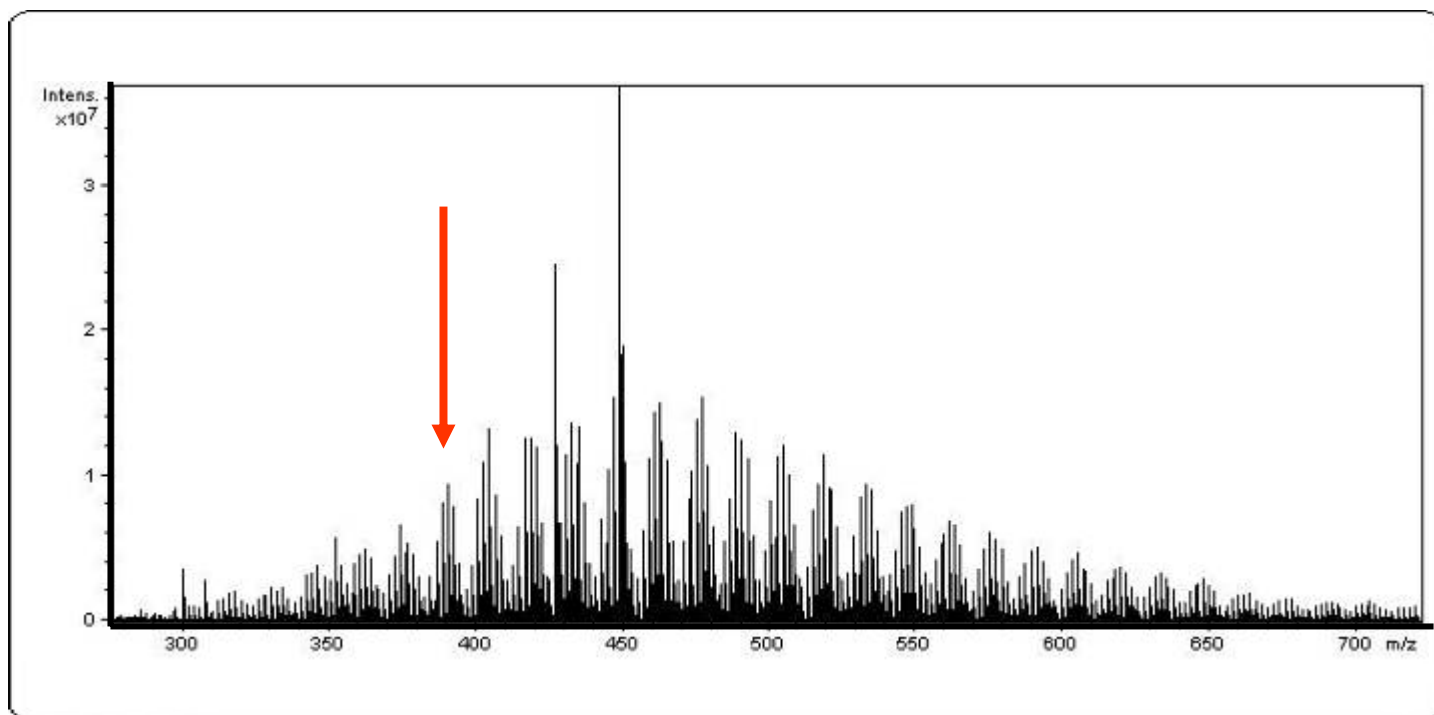
*1) Coupling to FT-ICR-MS*

*2) Coupling to size exclusion chromatography (SEC)*

*3) Comparison of extraction techniques*



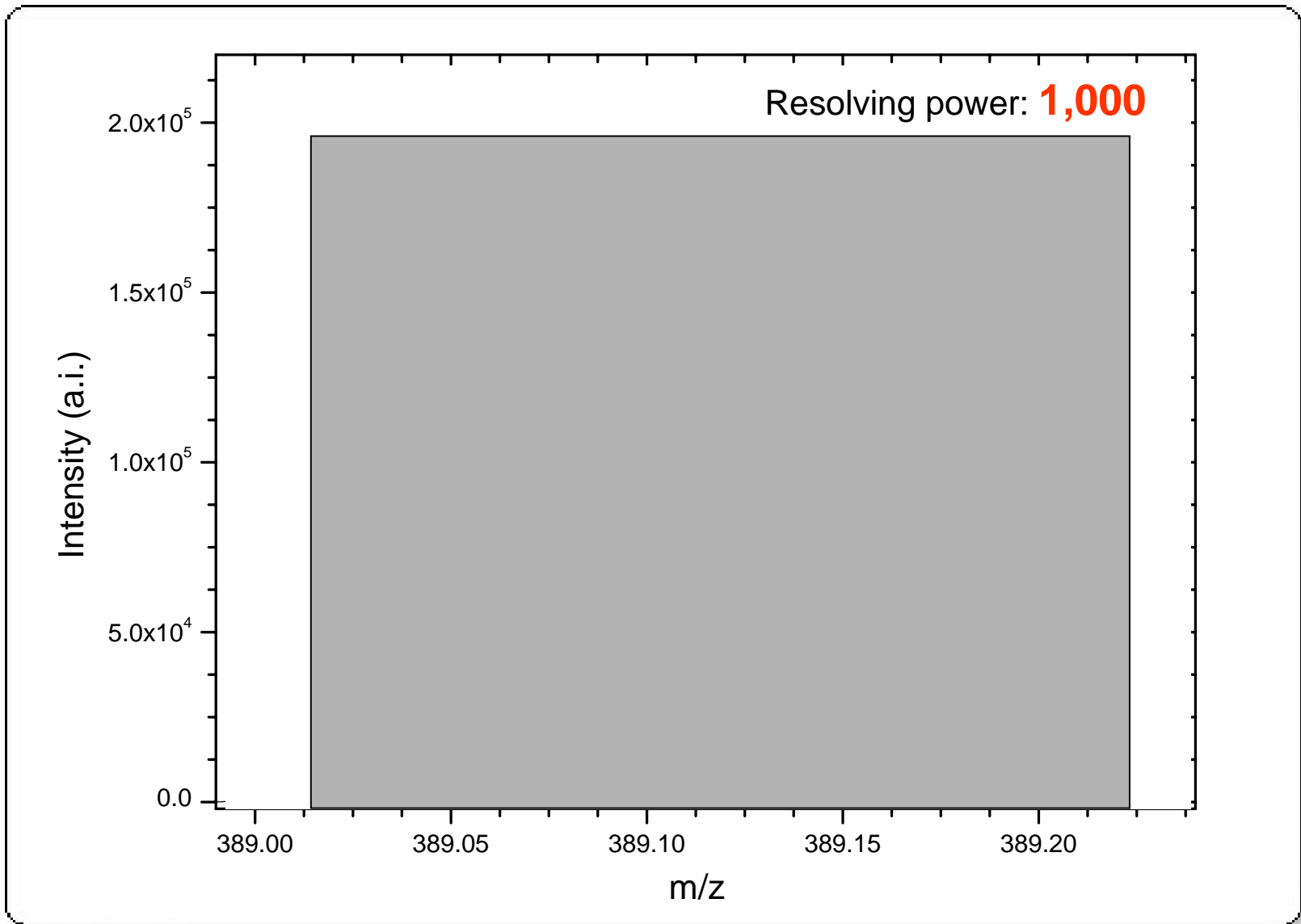
## Looking for biomarkers in marine DOM



Fourier-Transform  
Ion Cyclotron Resonance  
Mass Spectrometry (FT-ICR-MS)

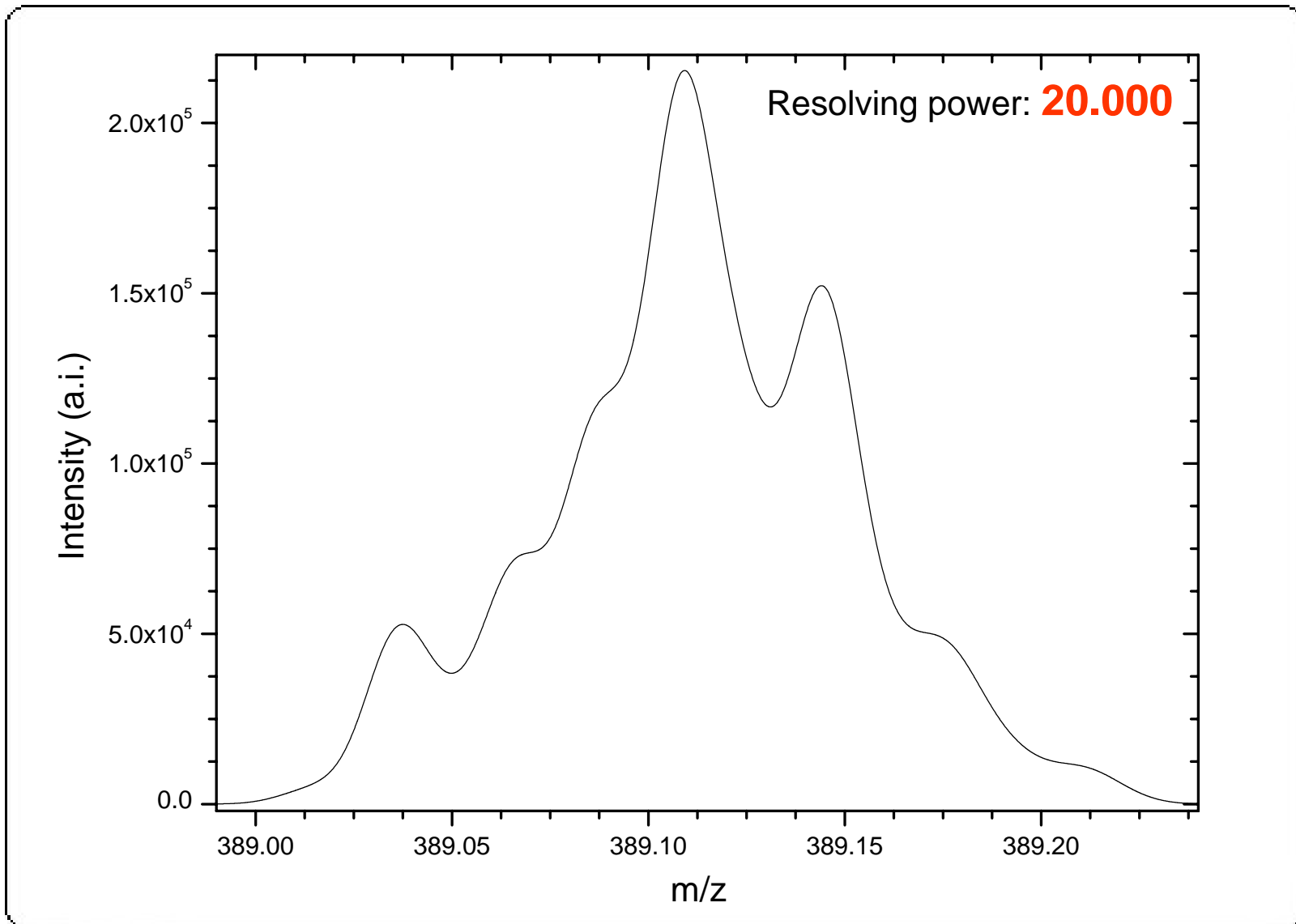


# Nominal Mass 389 m/z



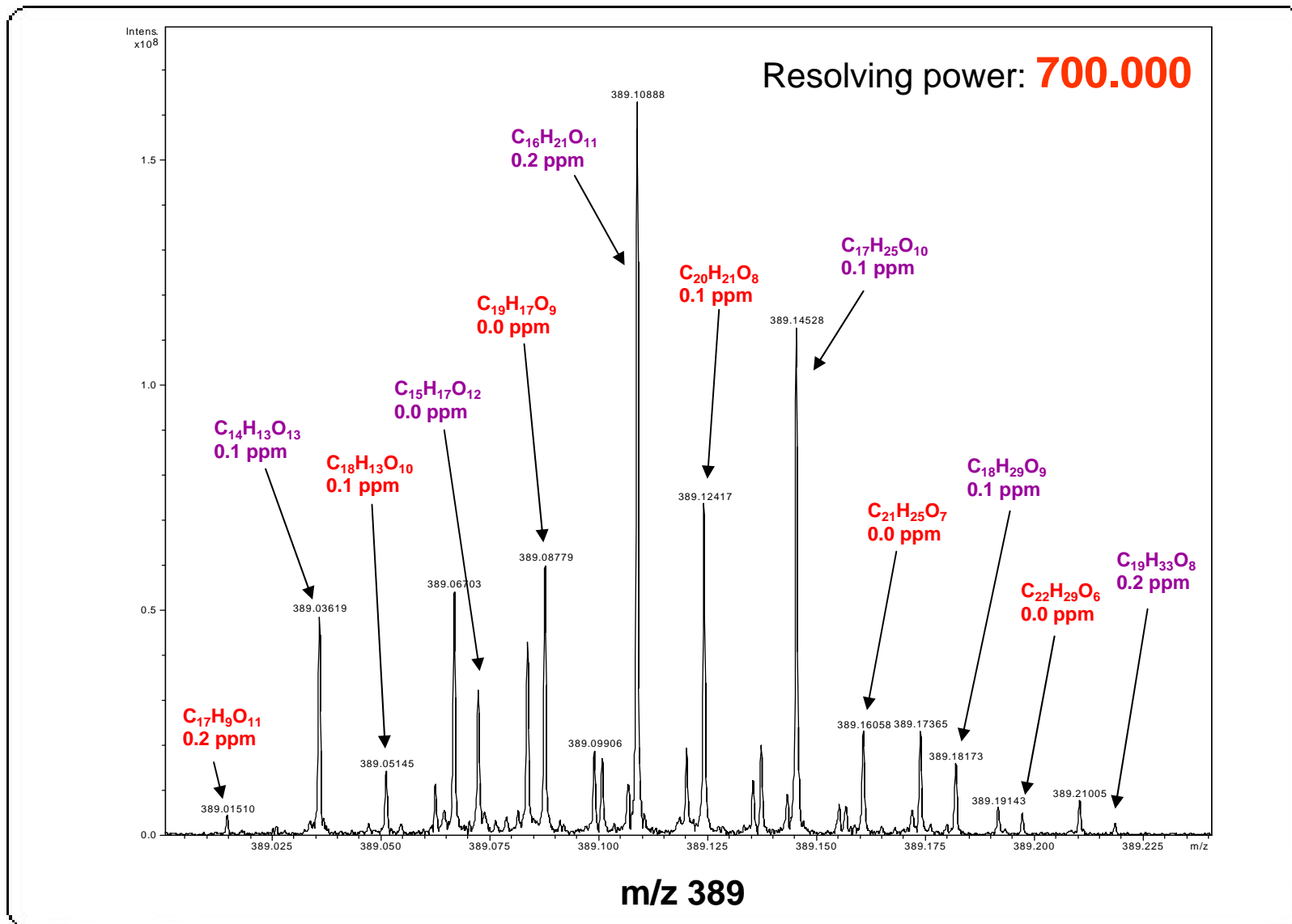


# Nominal Mass 389 m/z



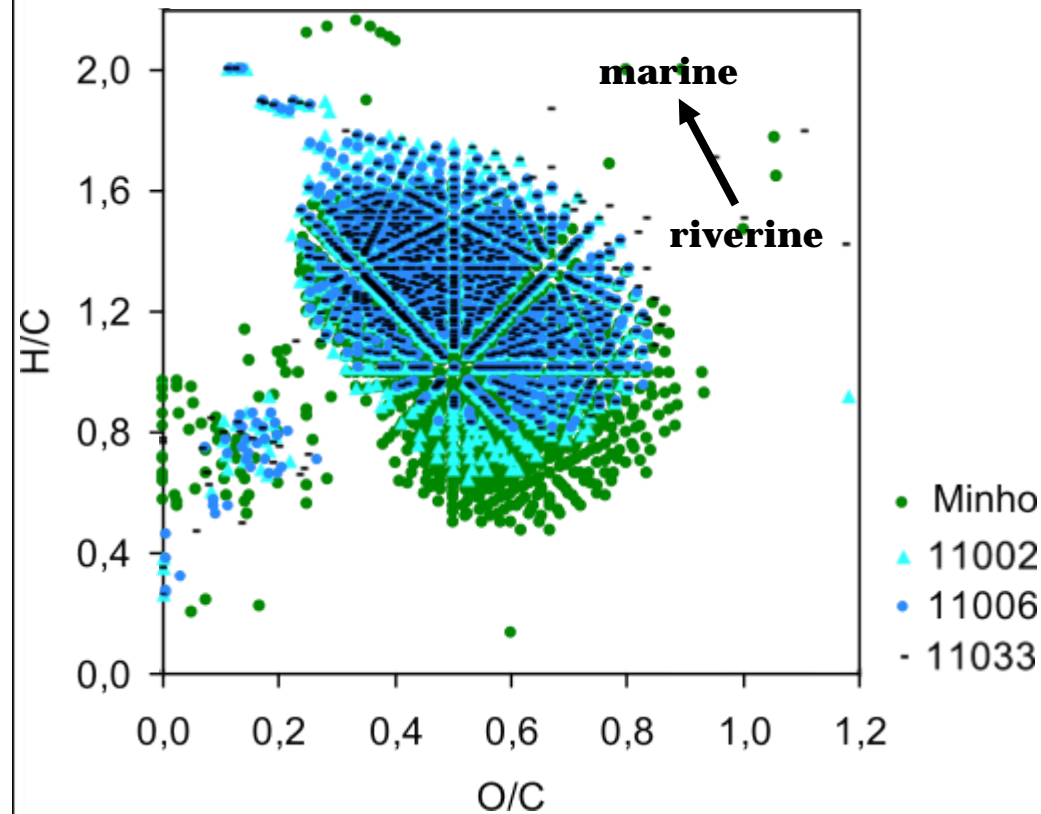


# Introduction: FT-ICR-MS

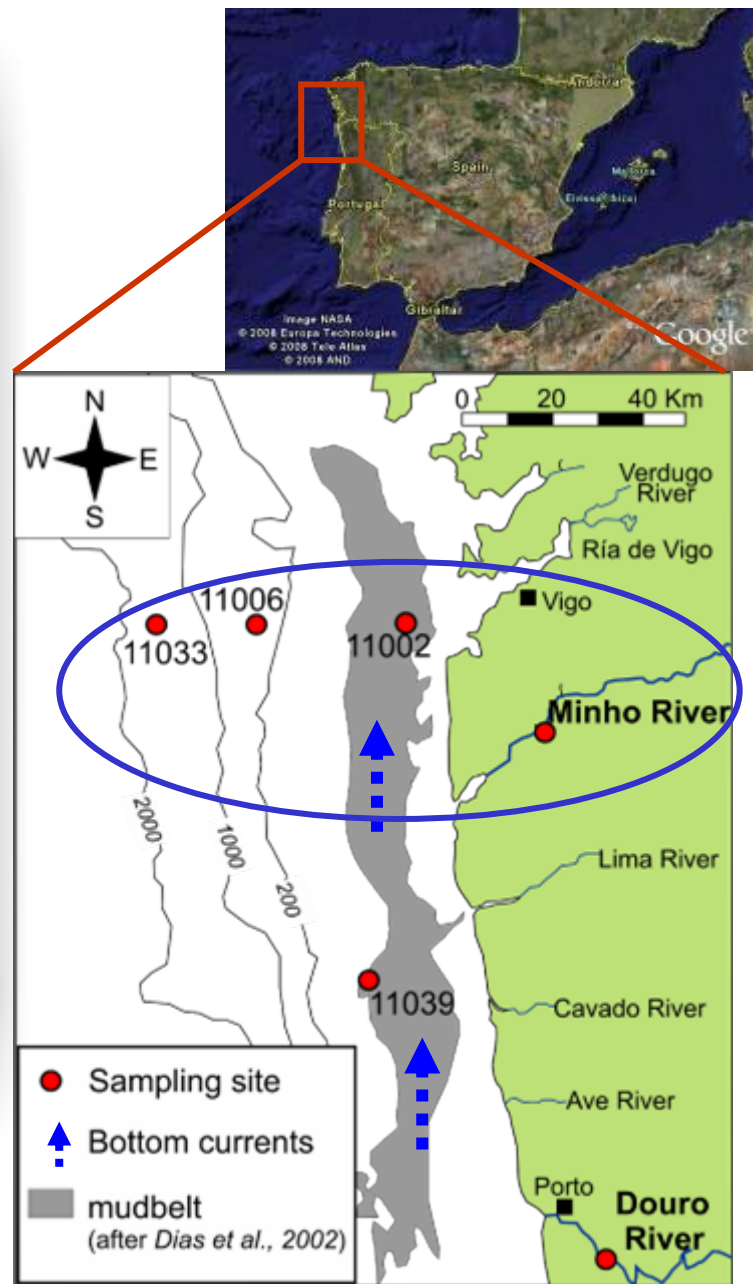


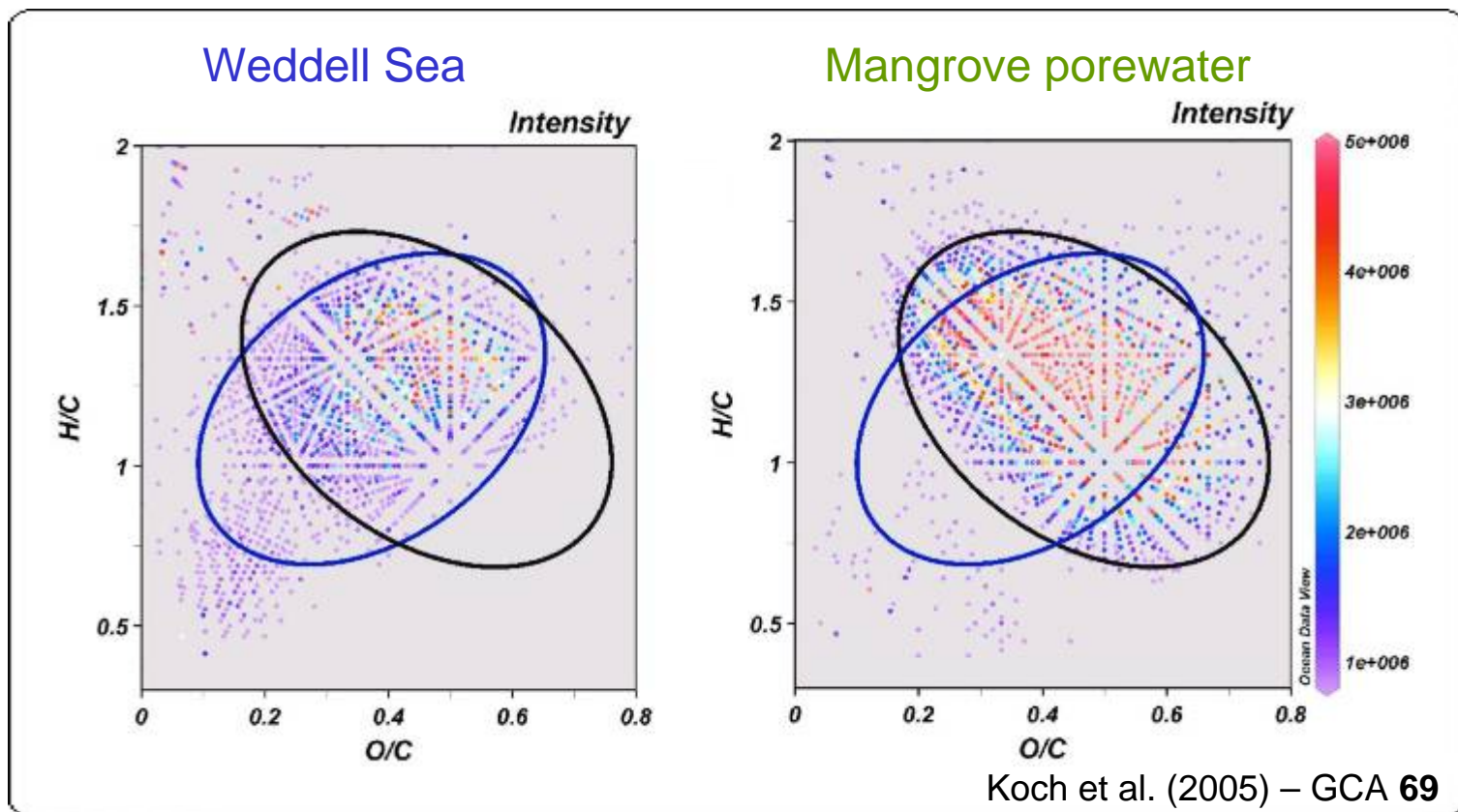
## Marine pore water: Portuguese Shelf

Van Krevelen Plot: Molecular element ratios

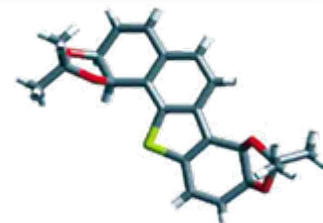


Schmidt et al. (in prep)





- Research aims:
- Targeted fractionation
  - Functional understanding
  - Decomplexation



Polarity-based chromatography might be helpful!





## Other examples:

**Microbial** fulvic acid diagenesis in groundwater:

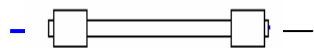
Einsiedl et al. (2007) *GCA*.

**Photodegradation** of mangrove DOM:

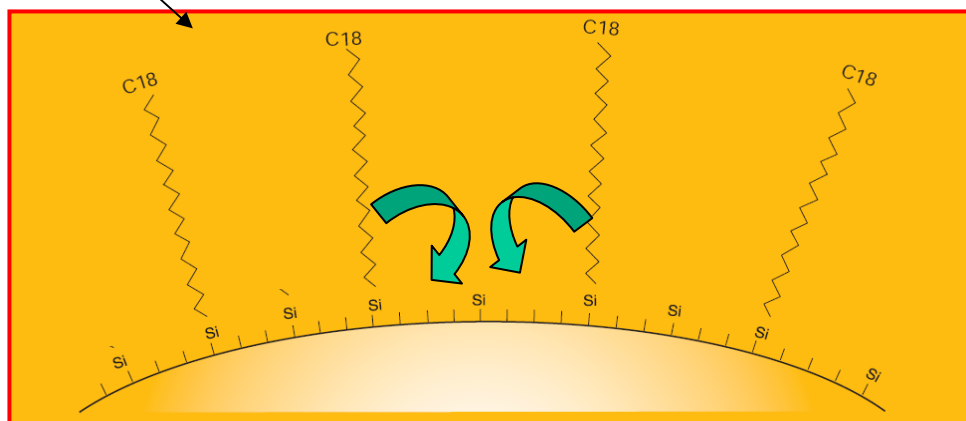
In prep.

**Polyaromatic hydrocarbons** in marine DOM

Koch and Dittmar (2006), *Rapid Communications in MS*.



Column



Regular Reversed phase C18 column

Eluent: Milli-Q-water with >2% of organic solvent

RP(C18)AQ-column with embedded polar groups

Eluent: Pure milli-Q-water

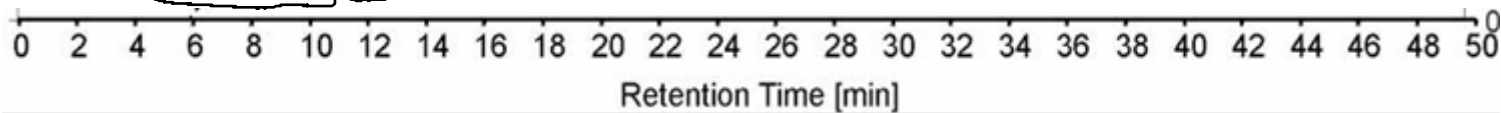
No collapsing of the C18-phase!



# Chromatography

20% MeOH

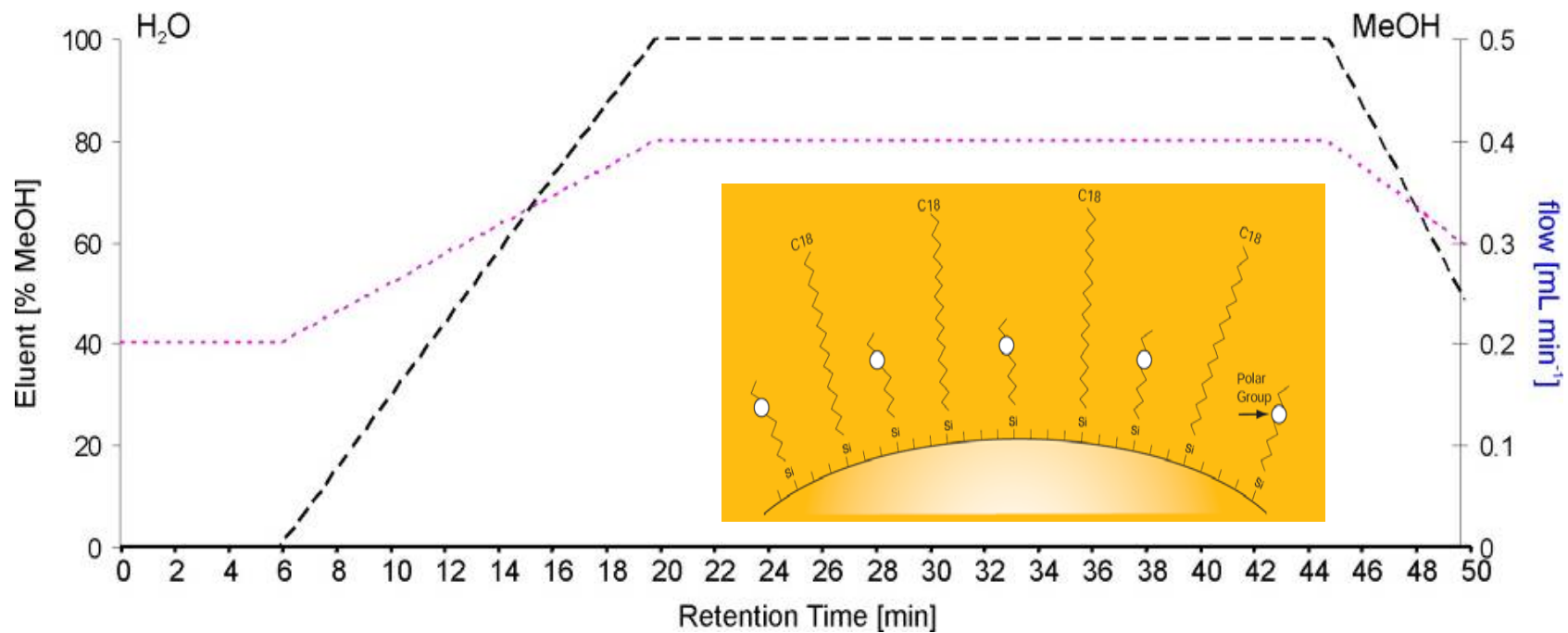
100% MeOH



Decreasing Polarity



# Chromatography

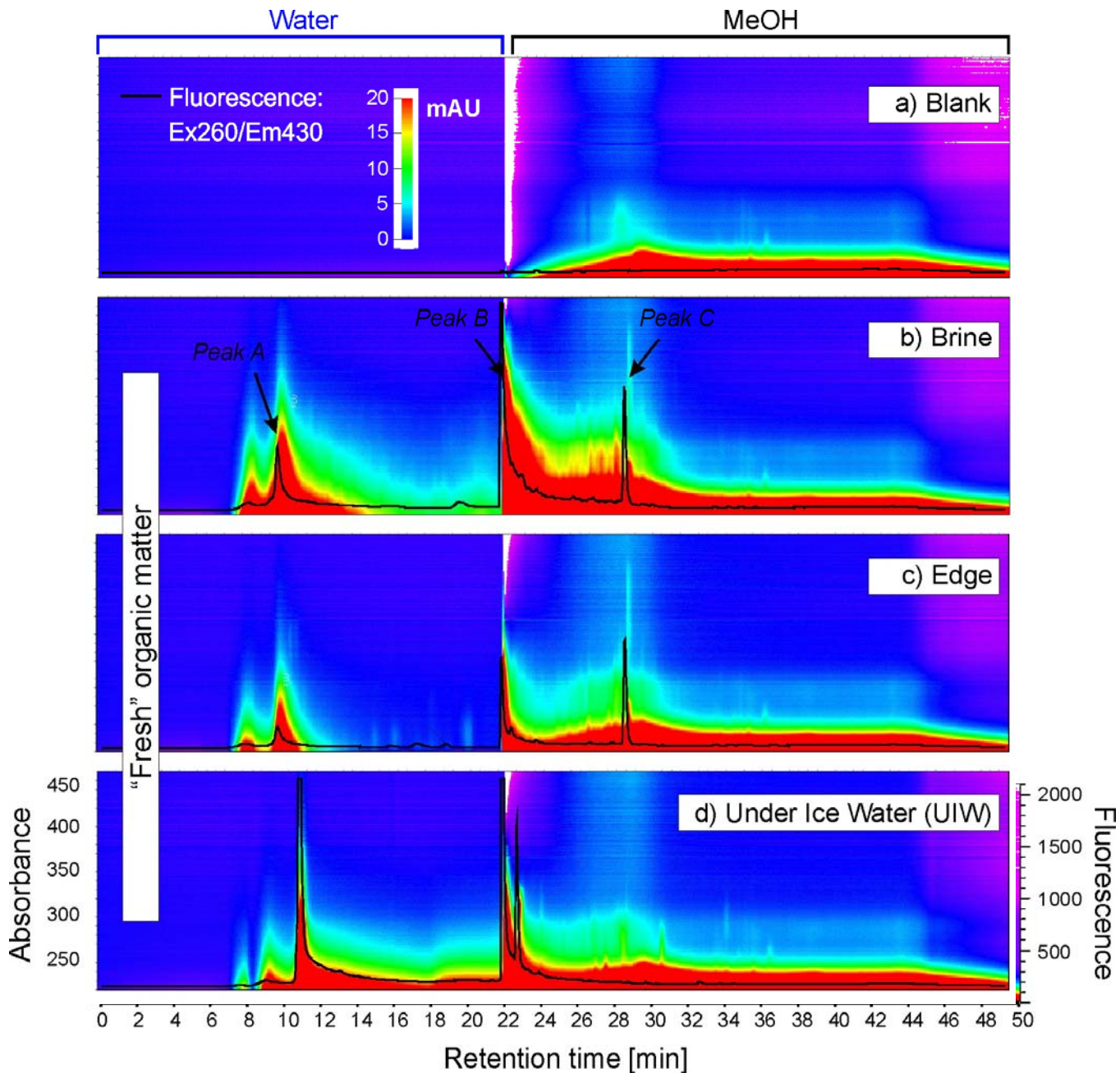


Decreasing Polarity



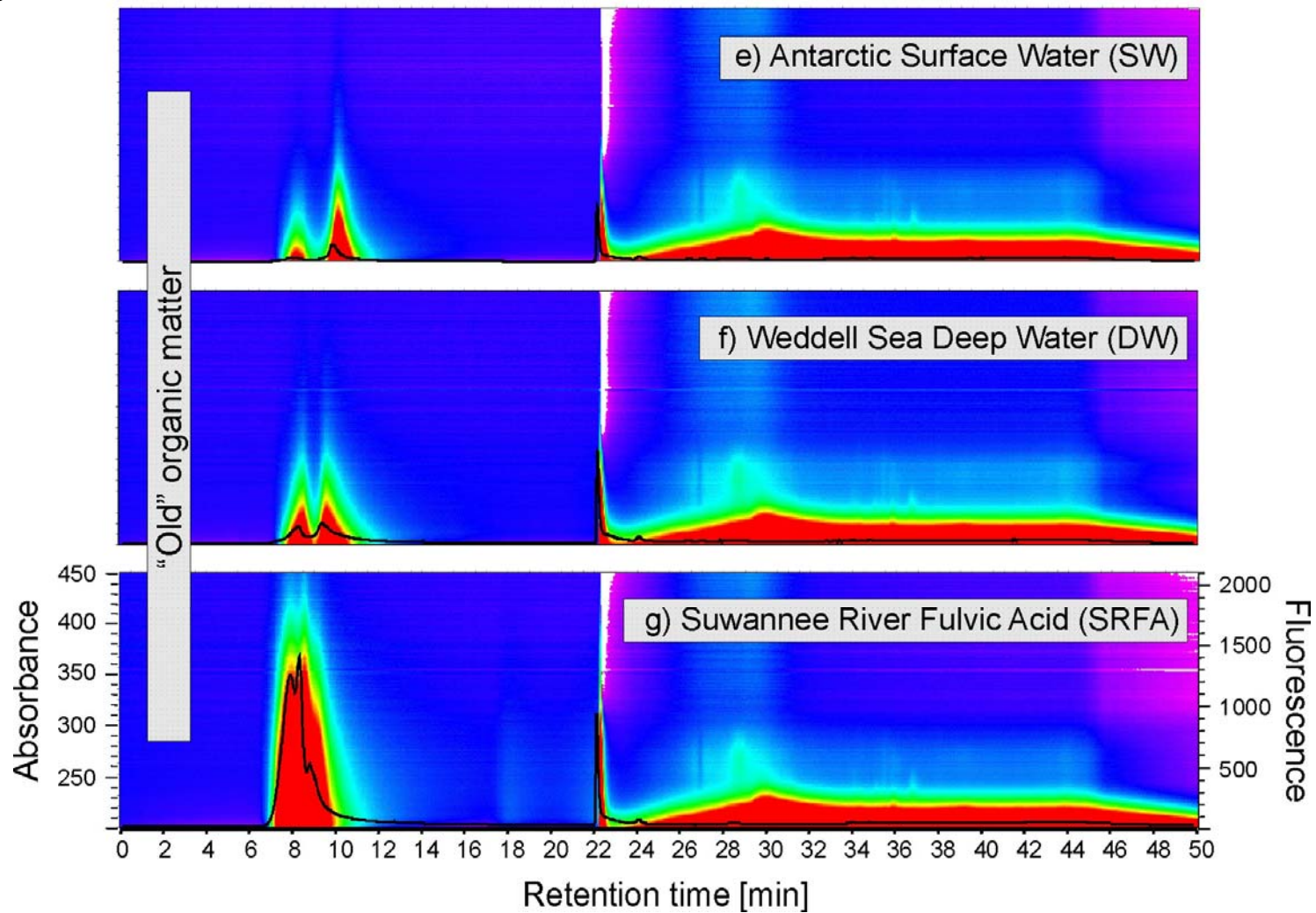
# Polarity separation of DOM

## Results



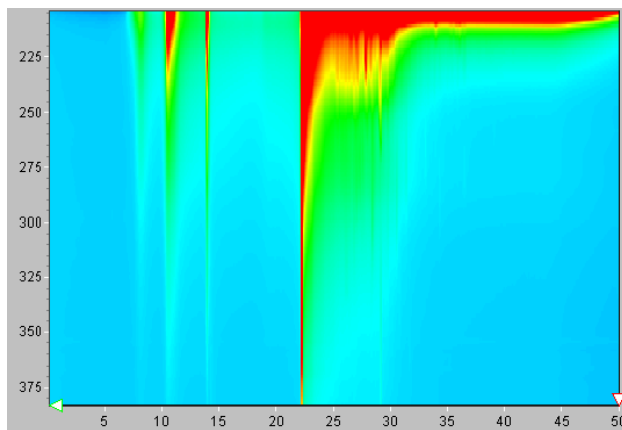


# Results

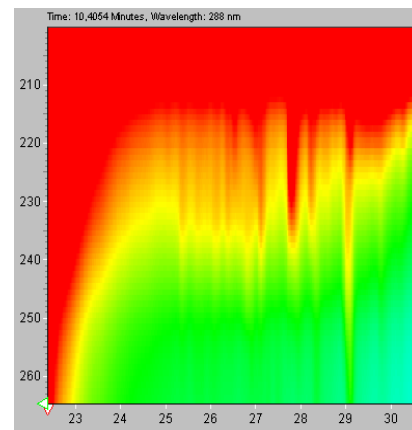


# Spectroscopic information

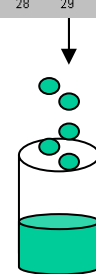
DAD contour plot



Detail

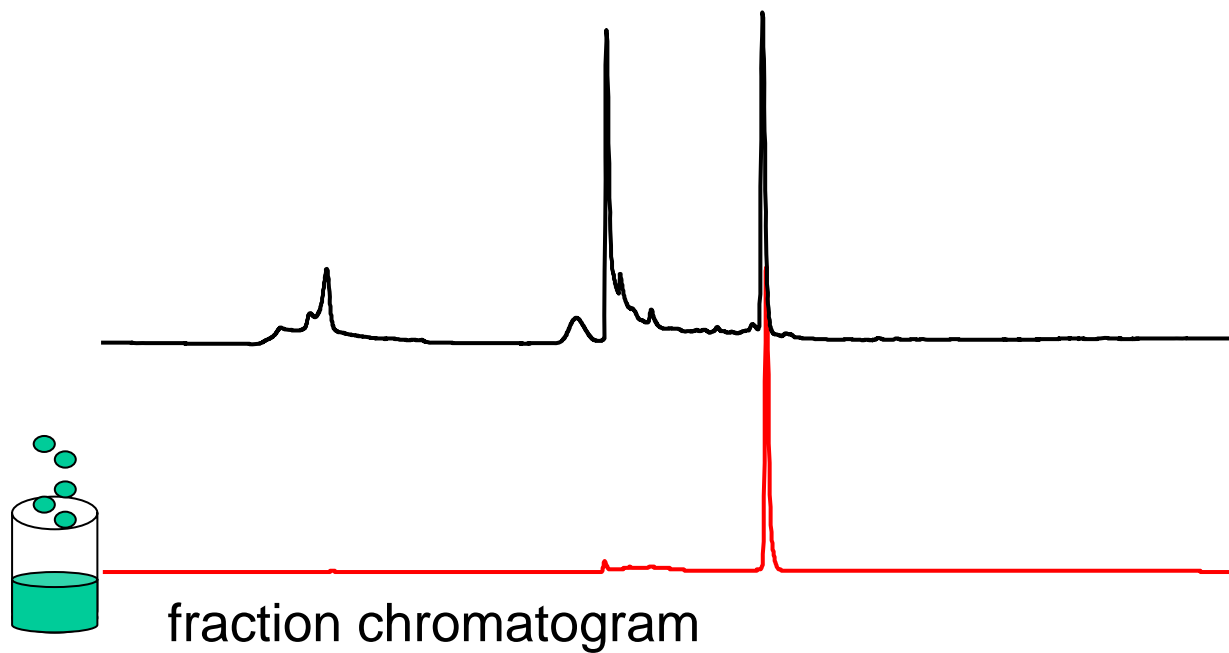


Fraction collector





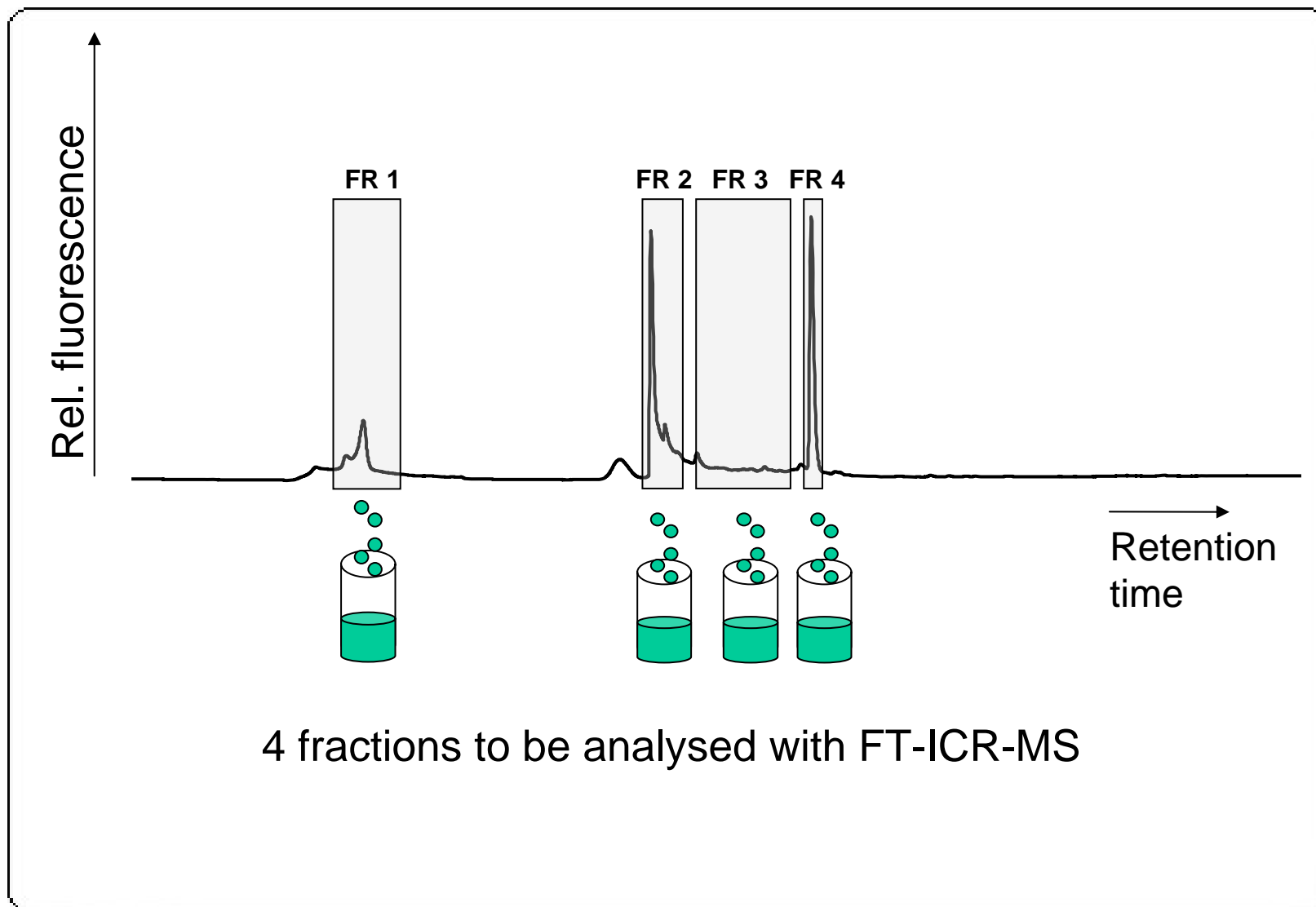
# Fractionation





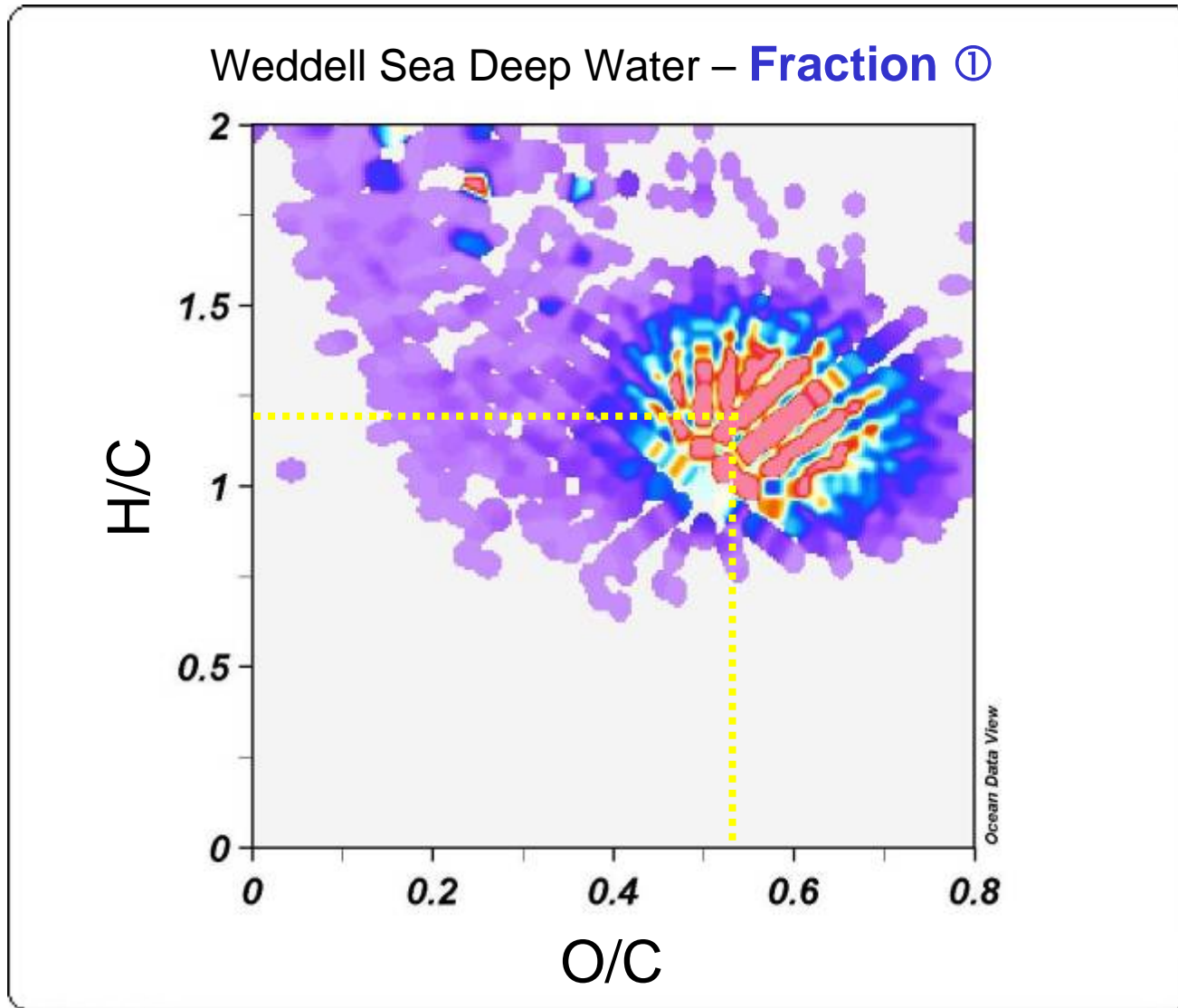


## Fractionation of DOM



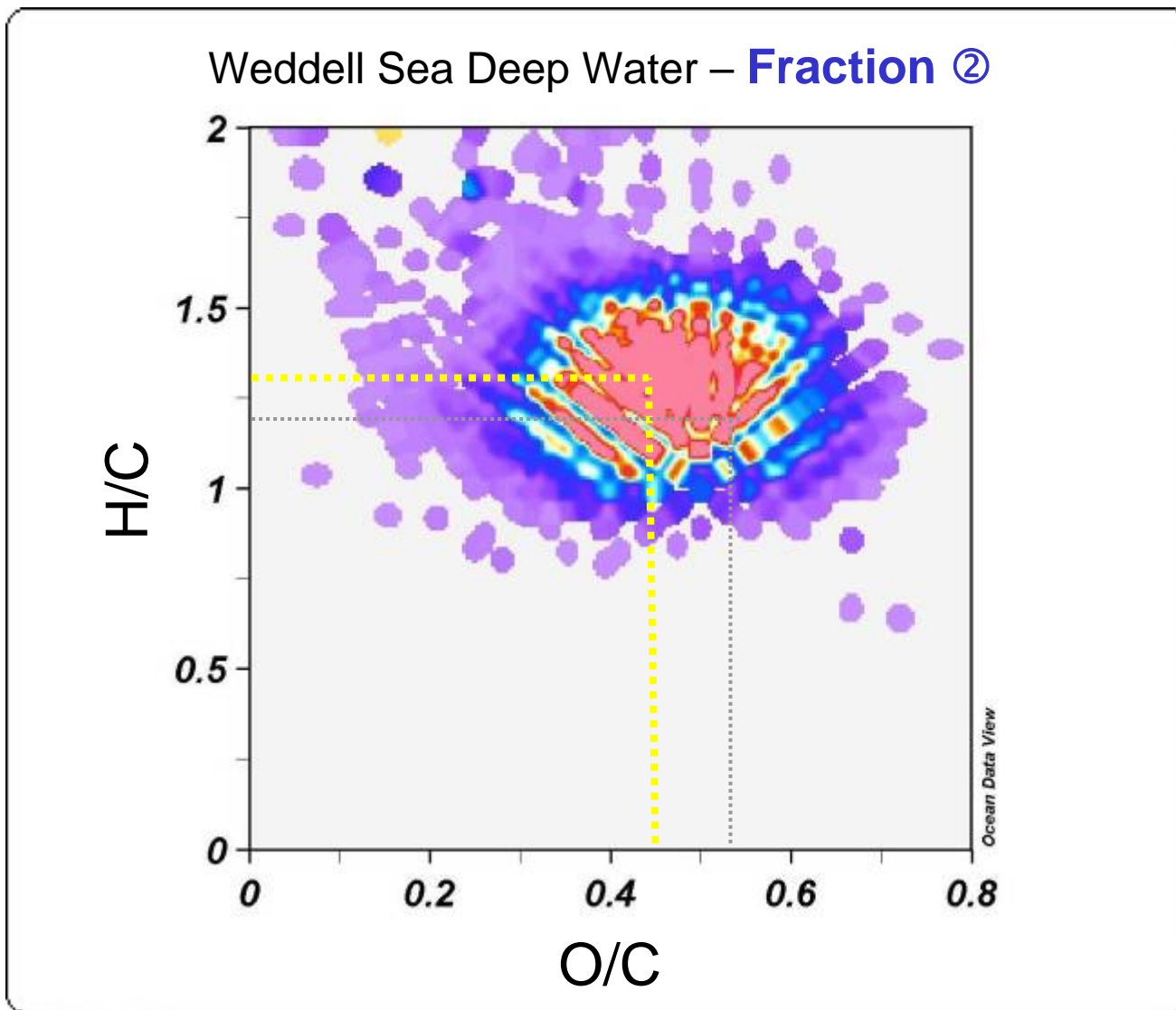


# Application 1: Offline-coupling to FT-ICR-MS



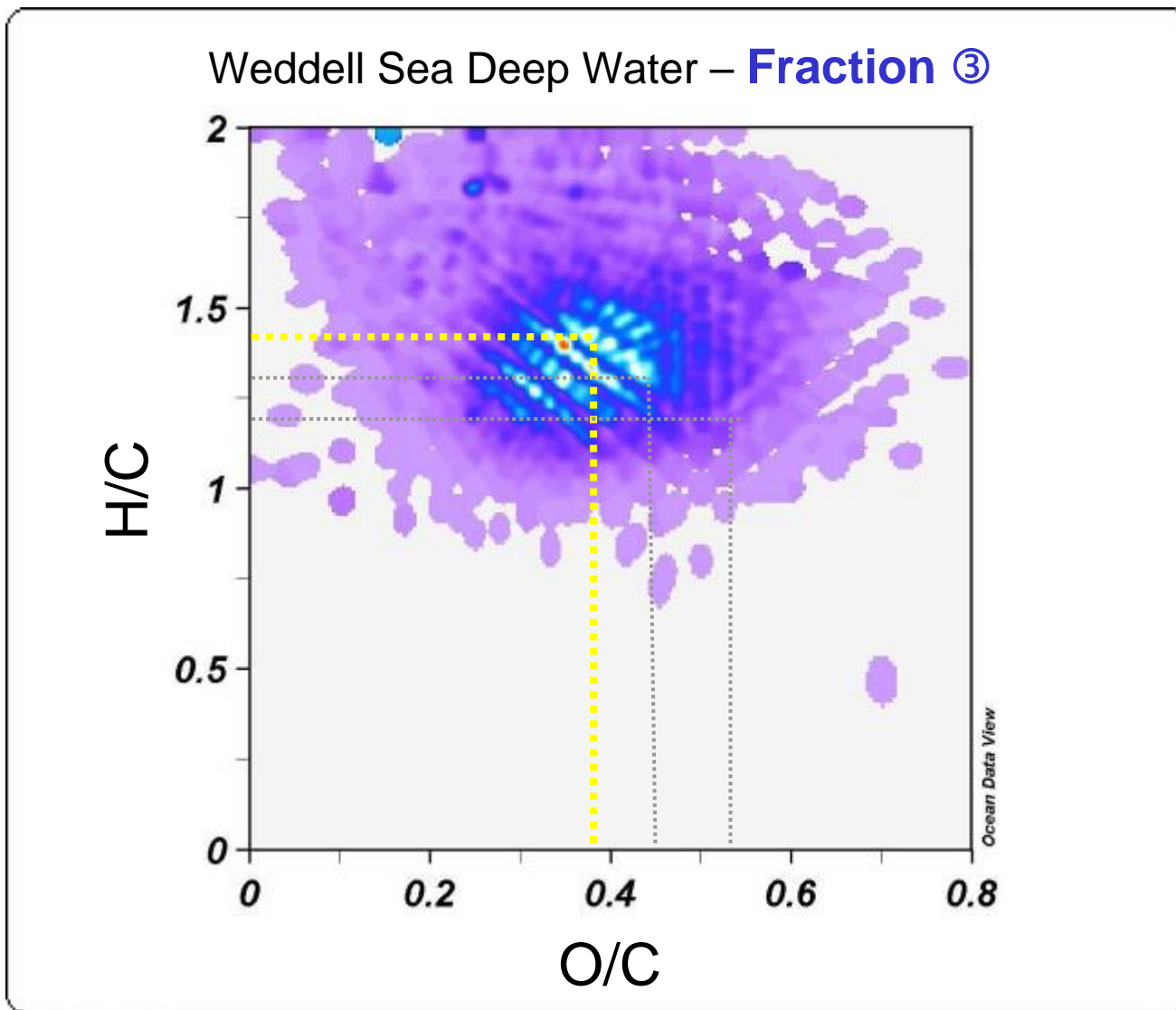
..... Intensity-weighted average, blank-corrected

CHO compounds, <600 m/z, ppm<0.5



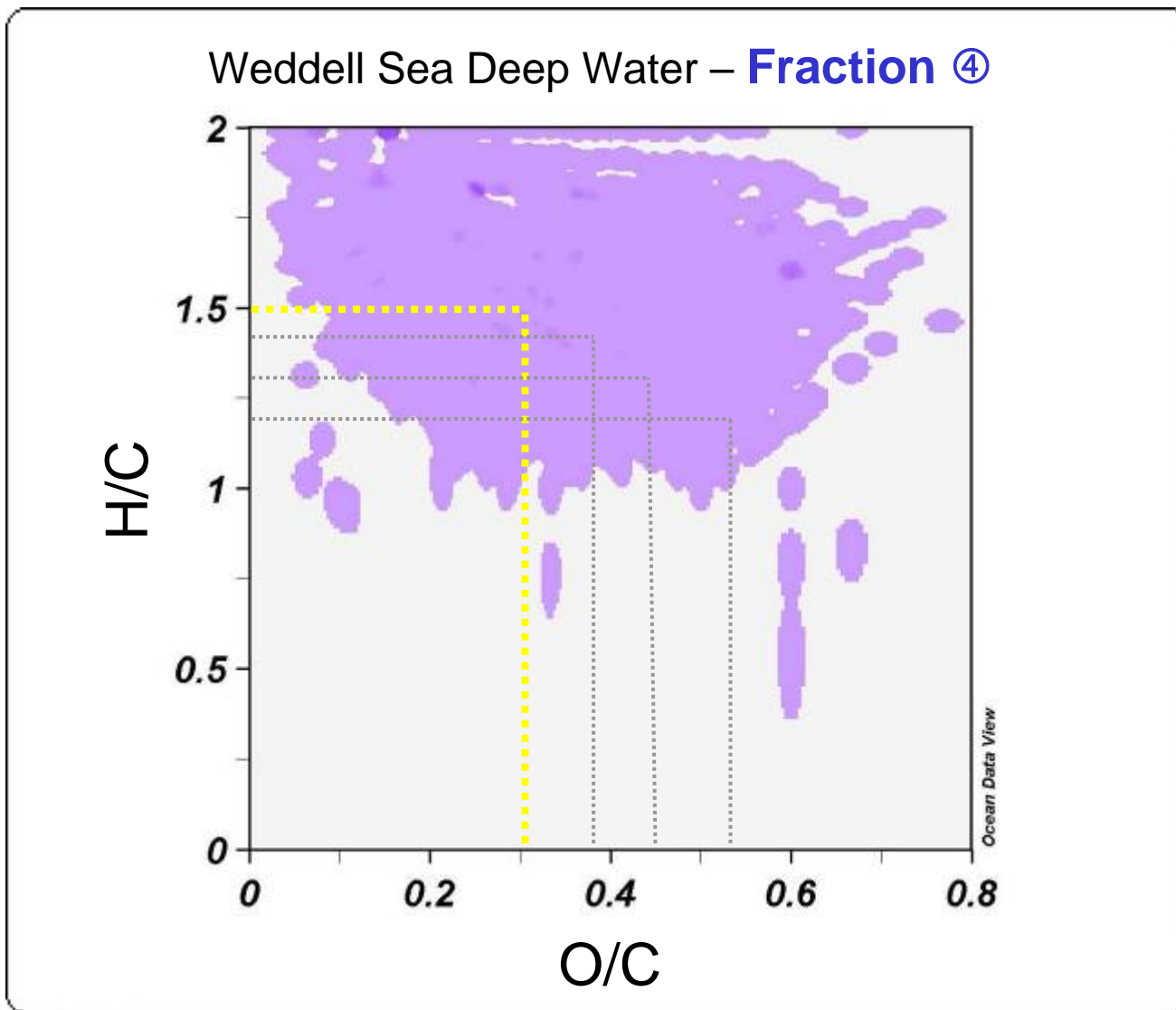
..... Intensity-weighted average, blank-corrected

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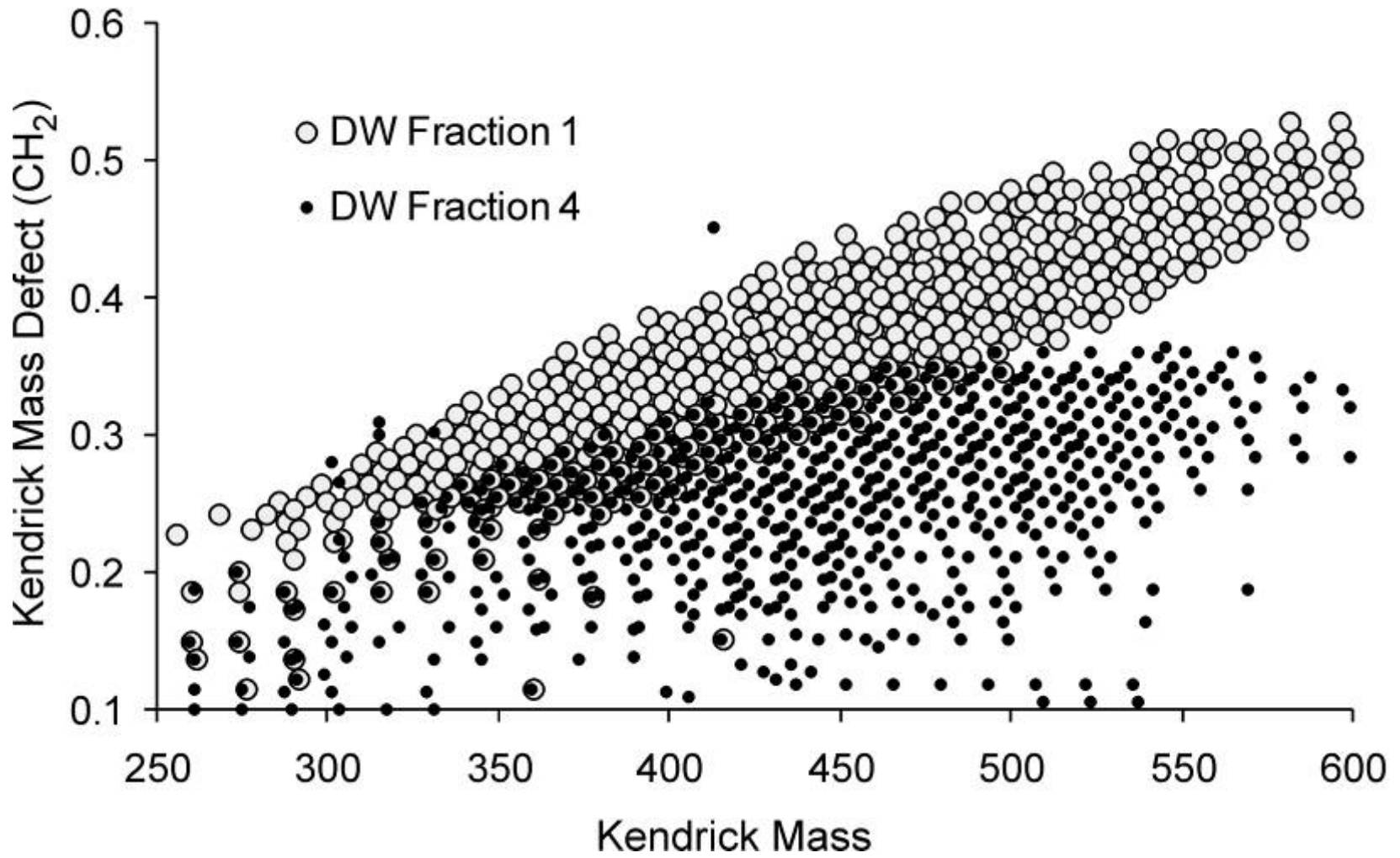


..... Intensity-weighted average, blank-corrected

CHO compounds, <600 m/z, ppm<0.5

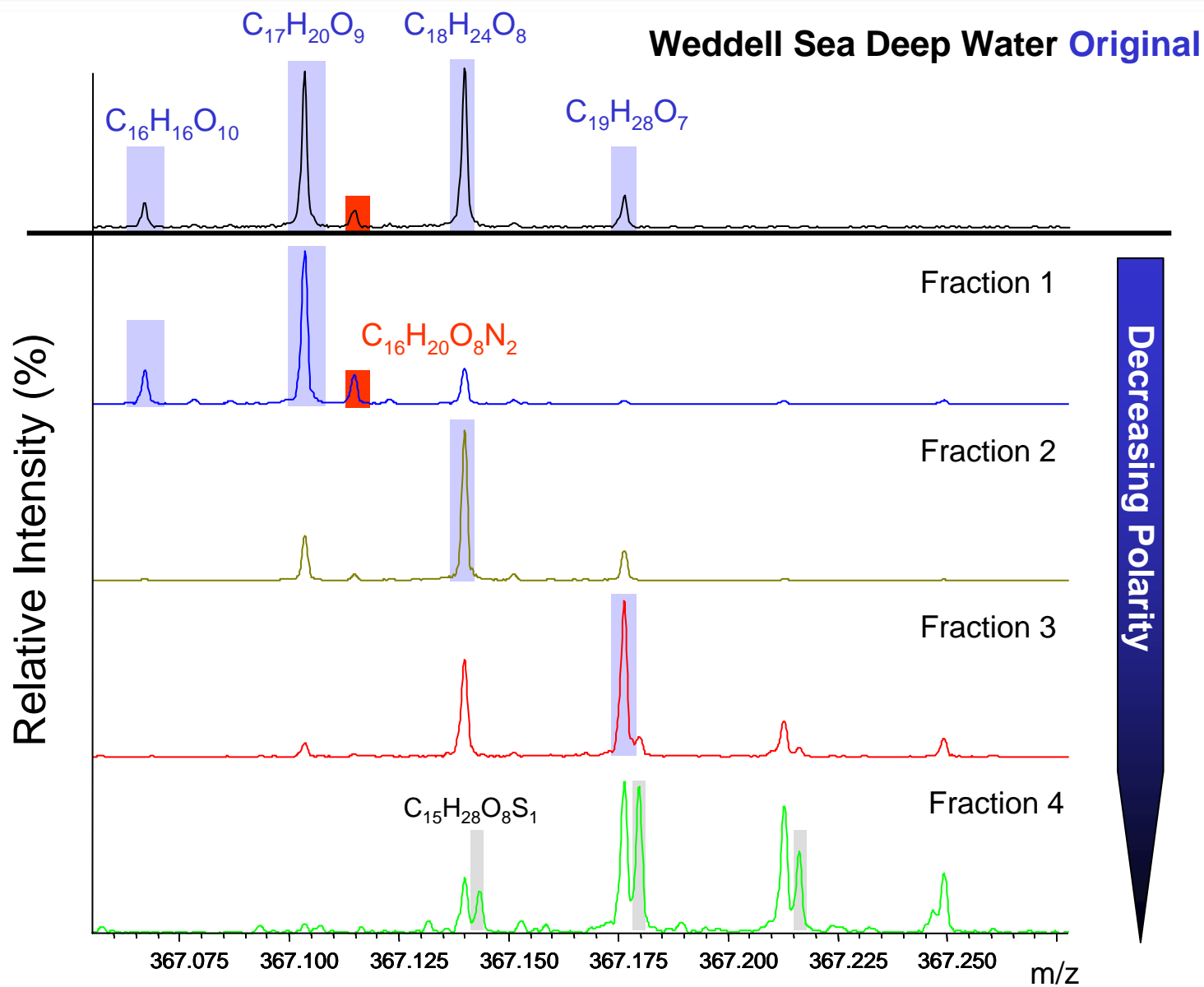


# Application 1: Offline-coupling to FT-ICR-MS

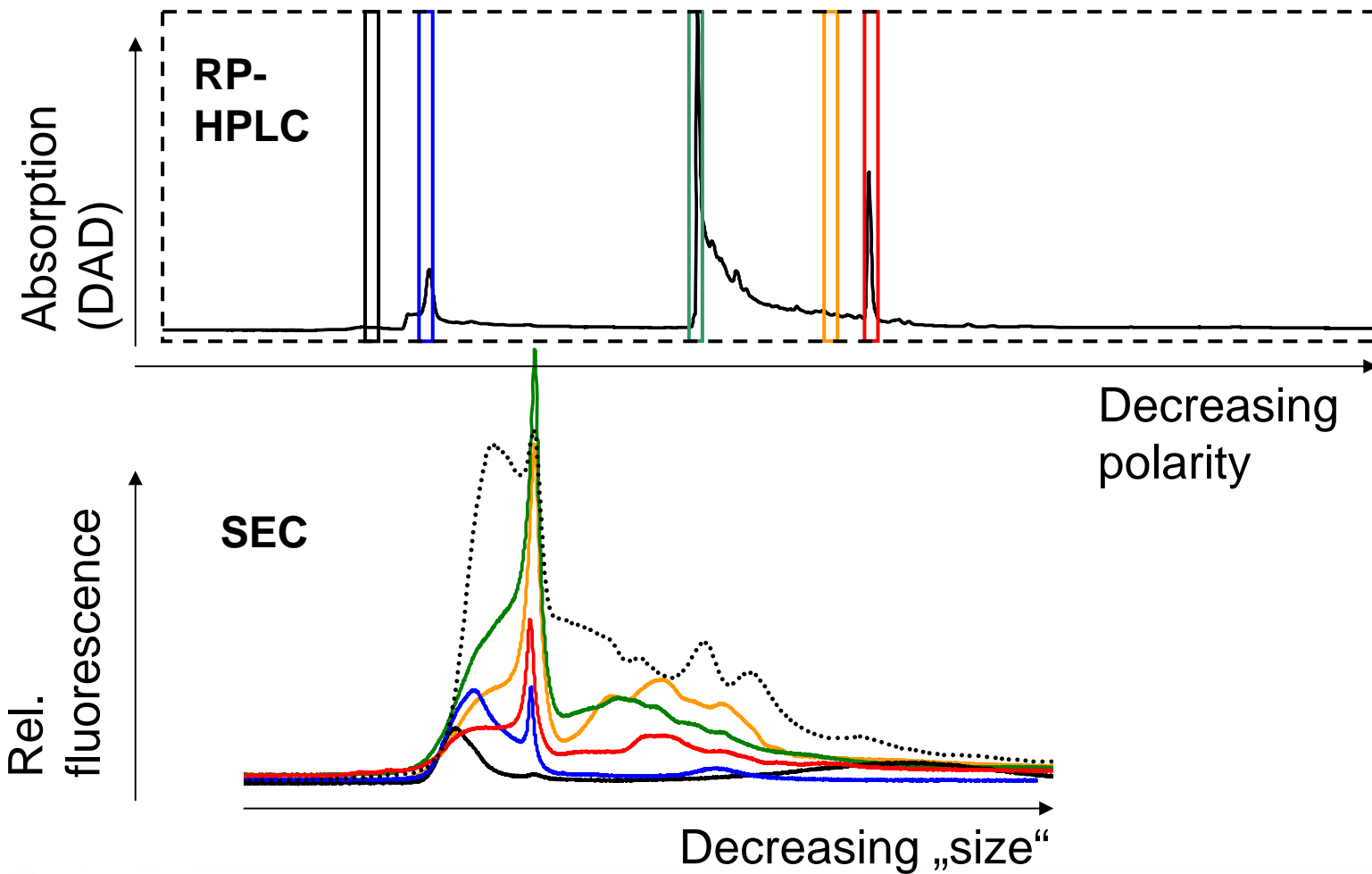




# Application 1: Offline-coupling to FT-ICR-MS



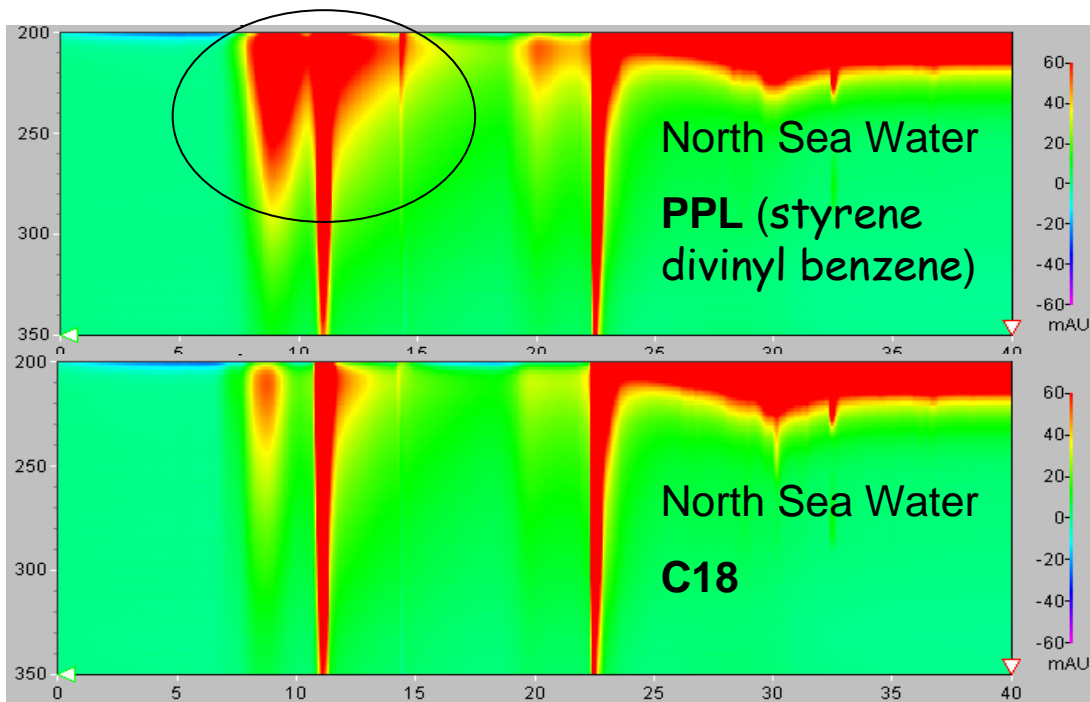
# Online-coupling RP-HPLC – Size exclusion chromatography







## Solid phase extraction



Minor requirements to analytical system



Standard method for DOM characterization.

Tool for fractionation and biomarker „picking“.

Very low salt concentration; no buffer



Sample enrichment for Mass Spectrometry.

Pure and comparable spectra in Fluoreszens-, UV/Vis- and IR-spectroscopy.

Many other applications possible



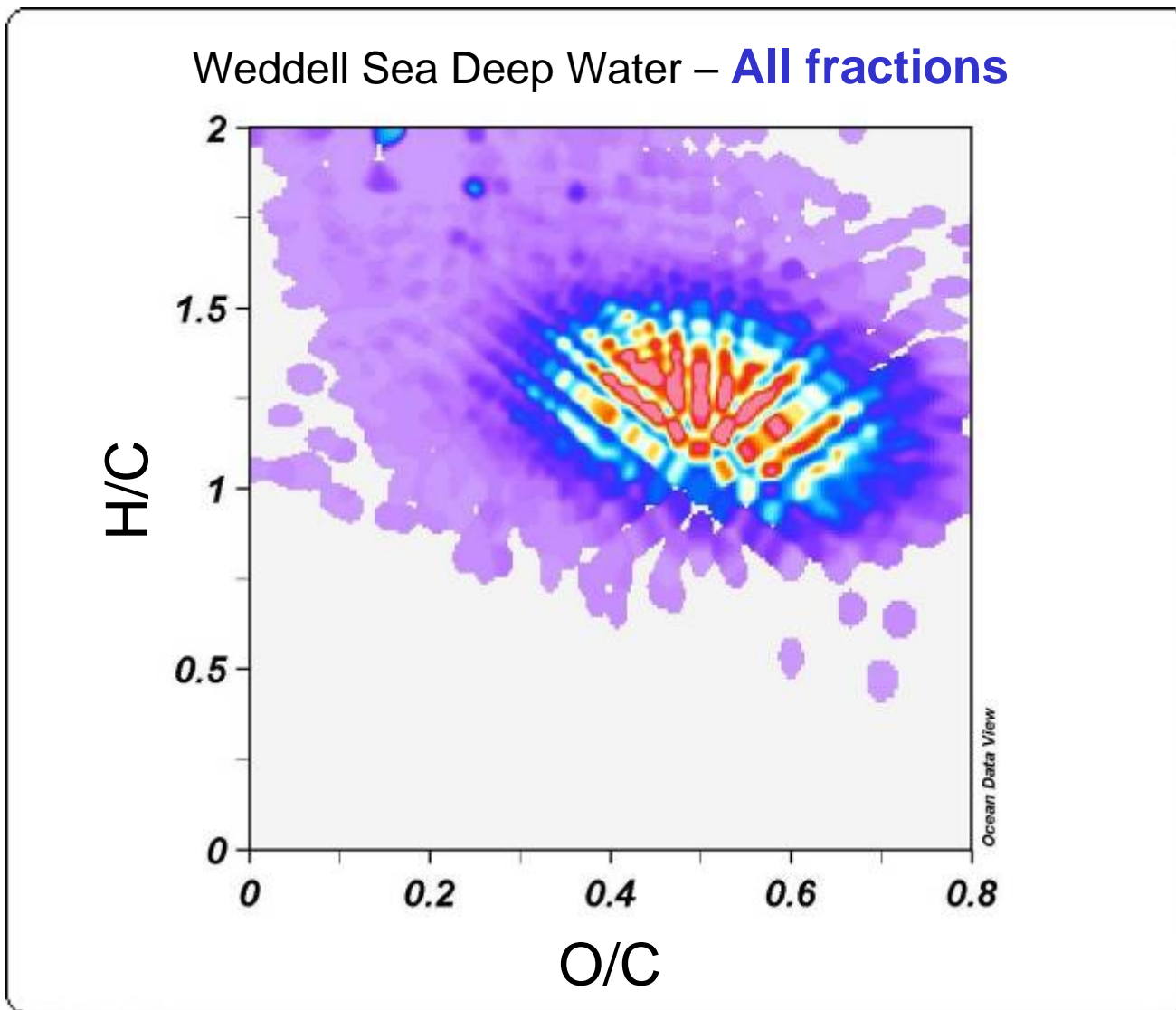
Combination with amino acid analyses or ICP-MS.

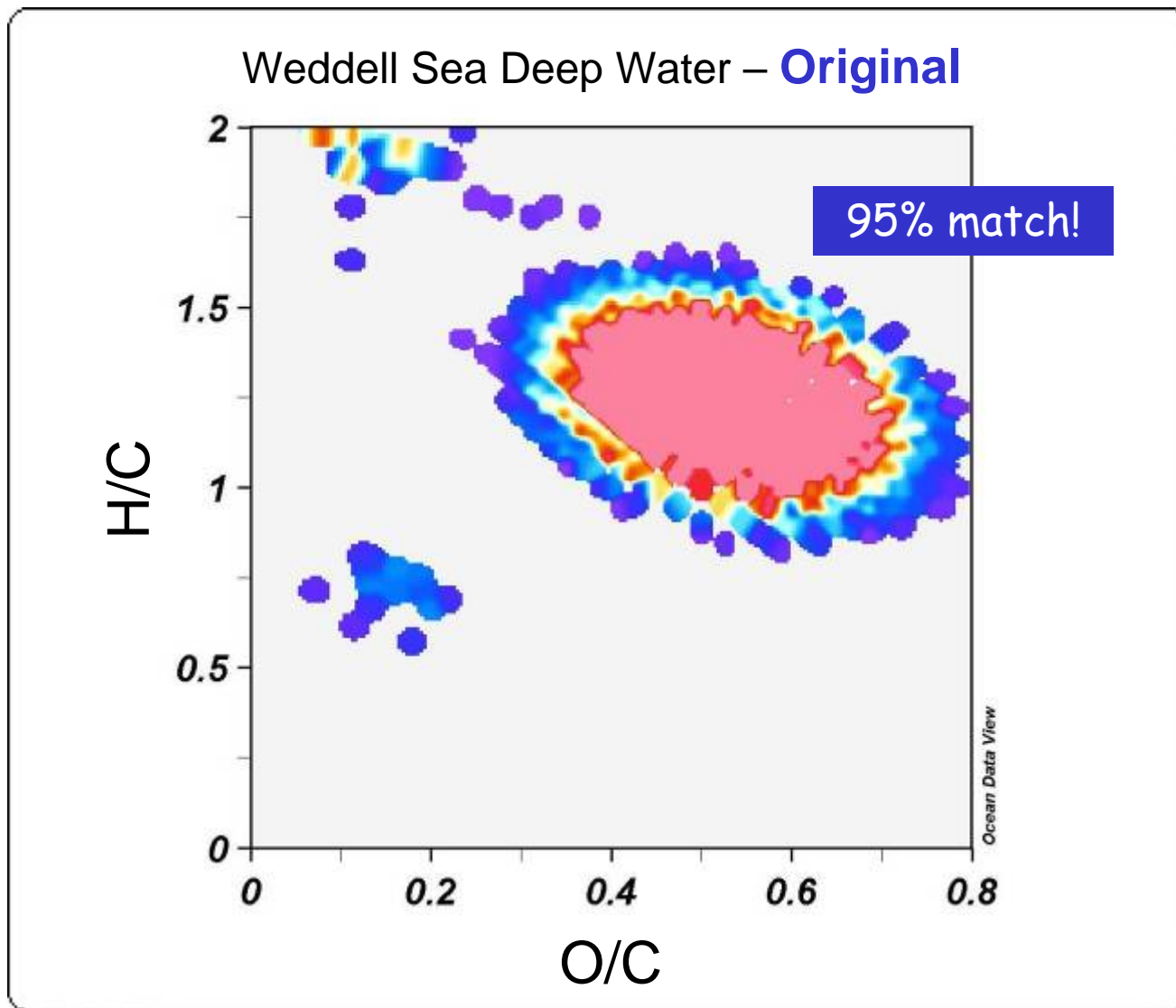


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Thank you for your attention!

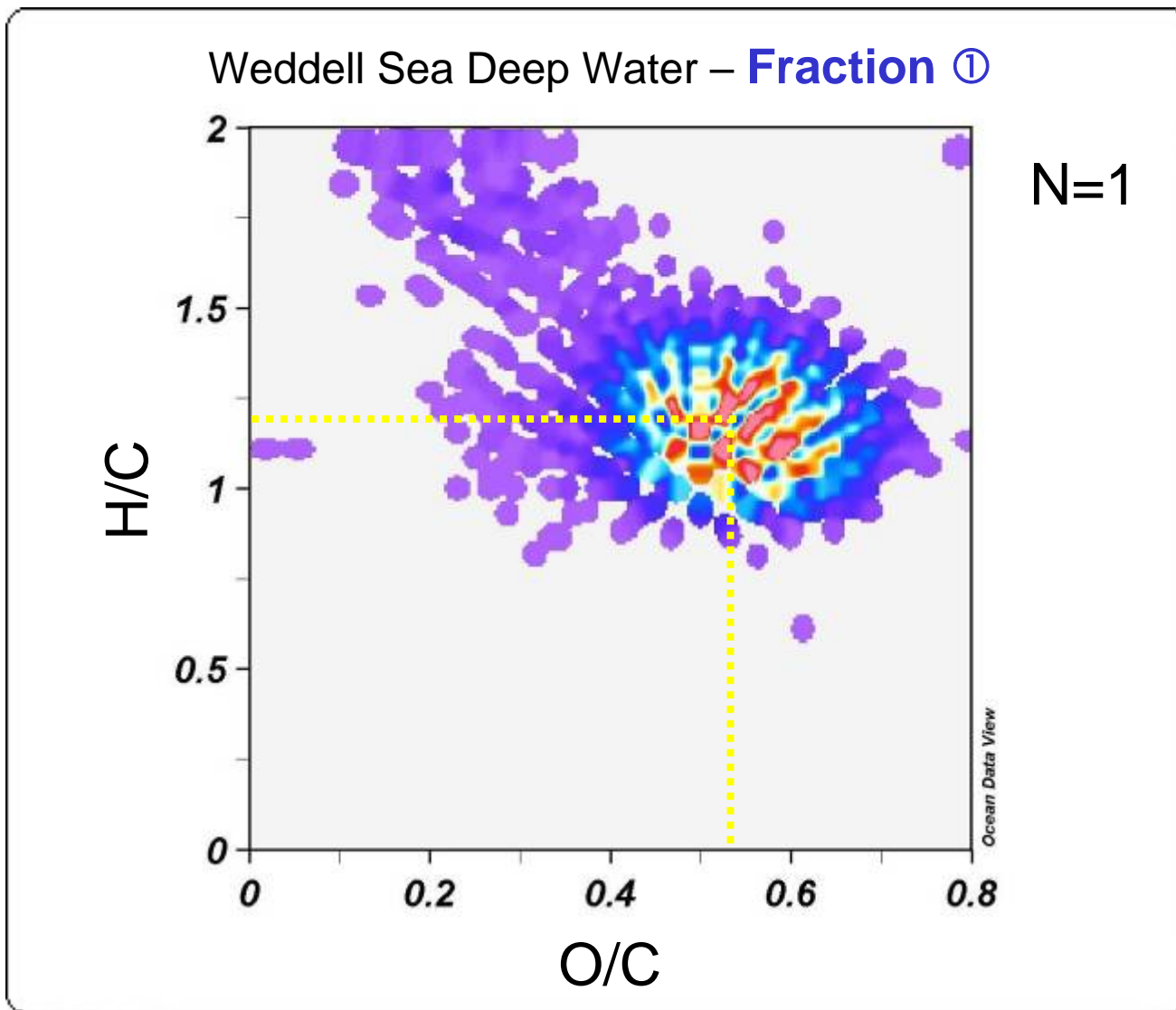
Sunset, Huangshan Mountains



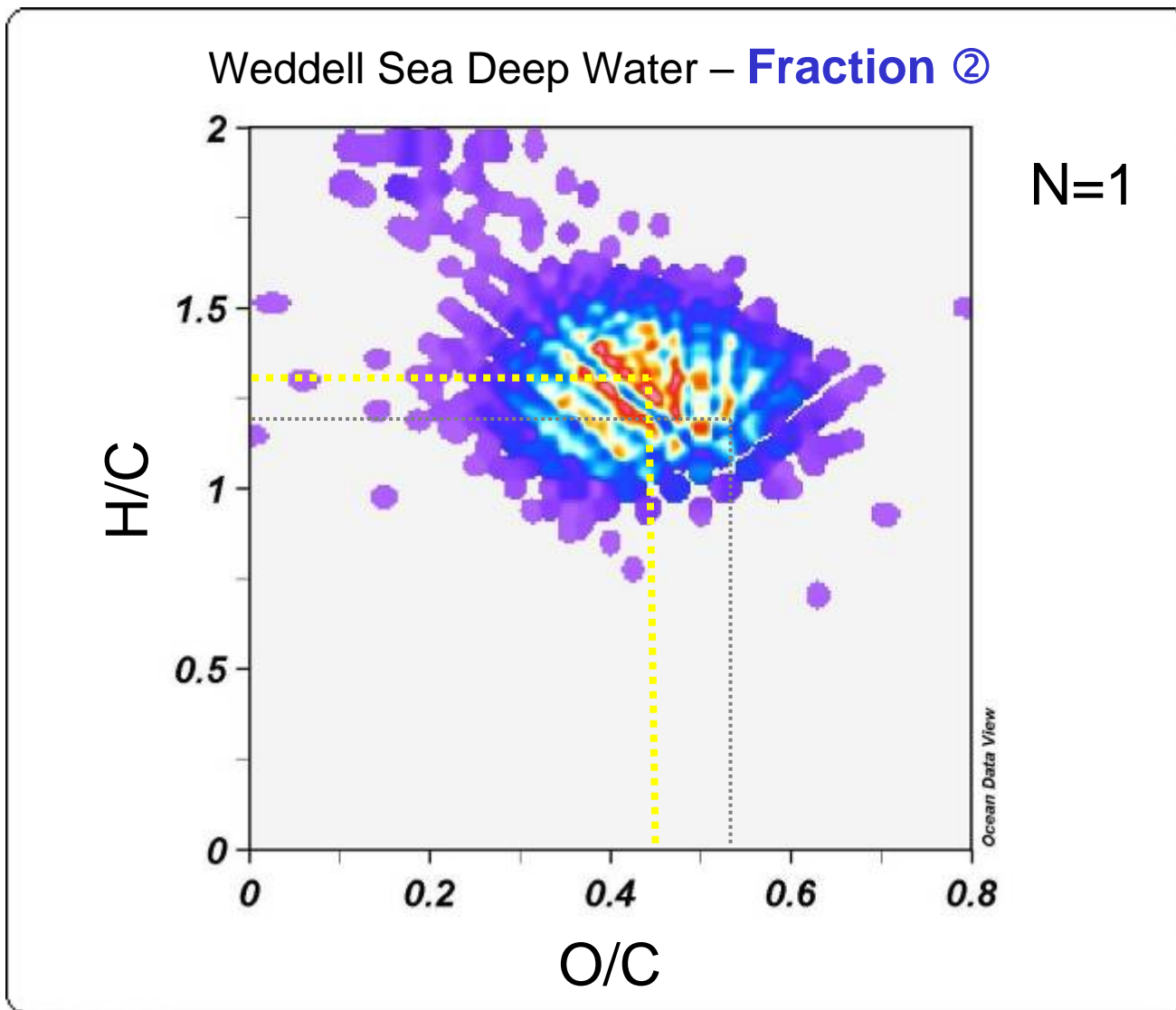




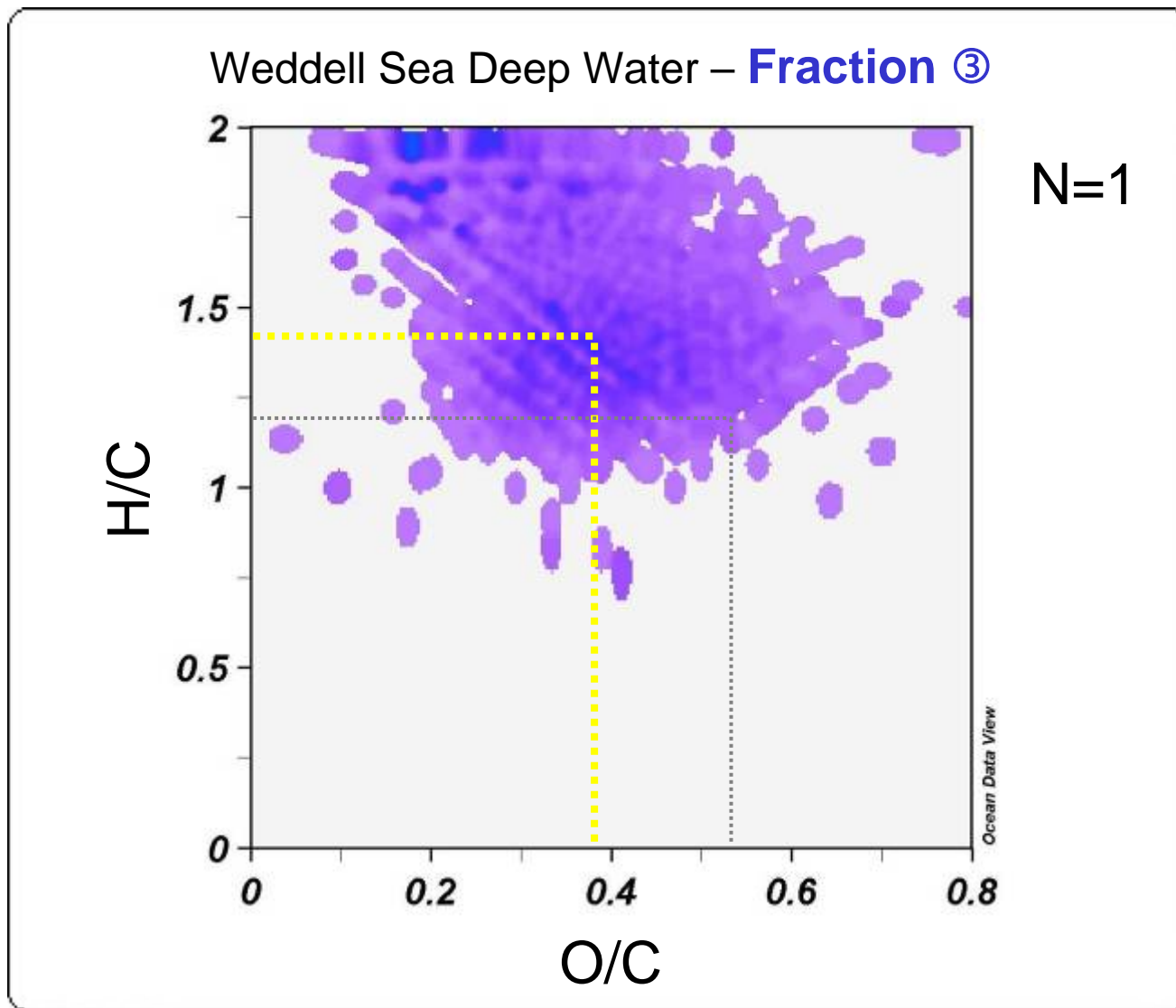
# Application 1: Offline-coupling to FT-ICR-MS



..... Intensity-weighted average, blank-corrected  $\text{CHON}_1$  compounds,  $<600 \text{ m/z}$ ,  $\text{ppm} < 0.5$



..... Intensity-weighted average, blank-corrected  $\text{CHON}_1$  compounds,  $<600 \text{ m/z}$ ,  $\text{ppm} < 0.5$

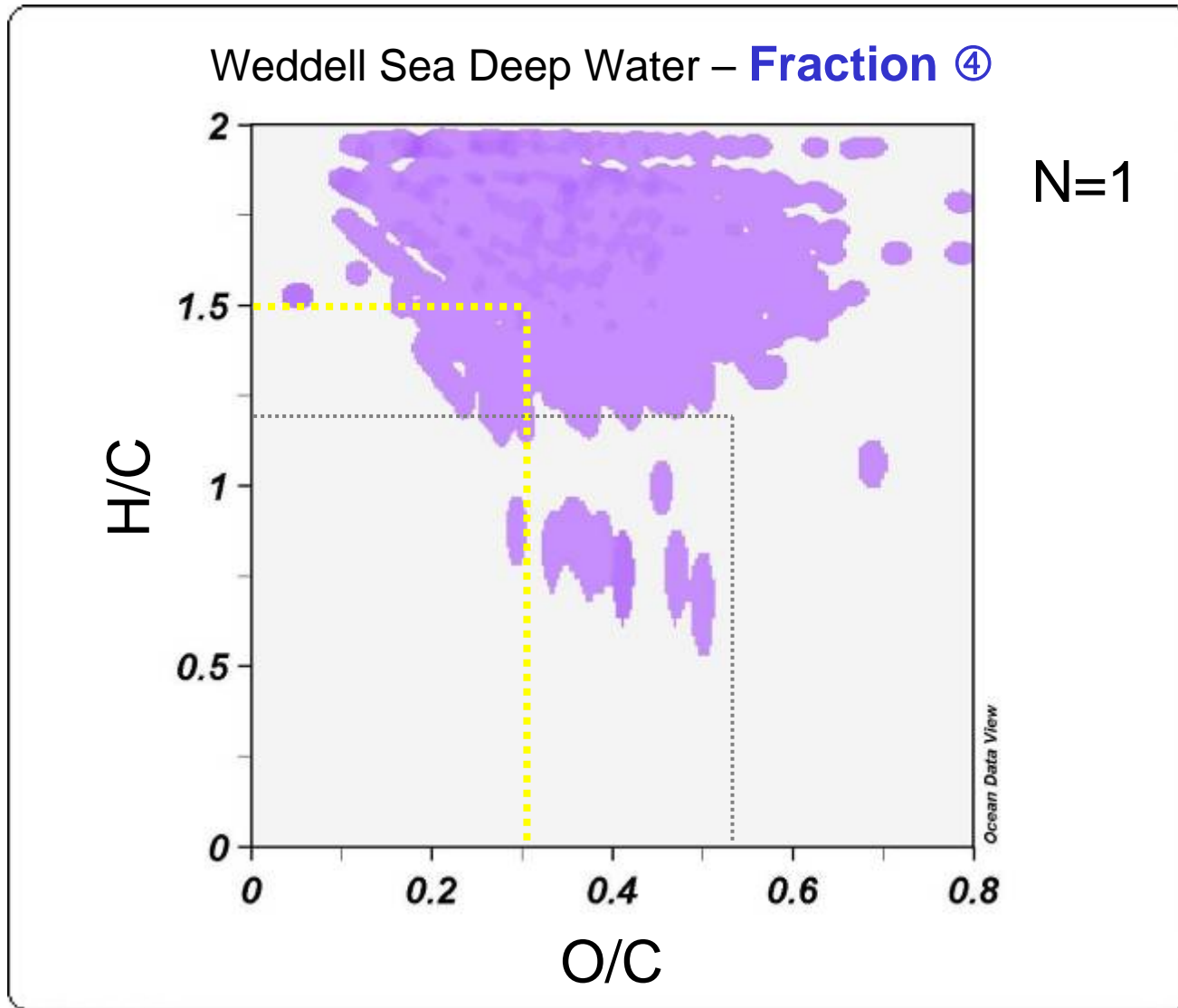


..... Intensity-weighted average, blank-corrected CHON<sub>1</sub> compounds, <600 m/z, ppm<0.5



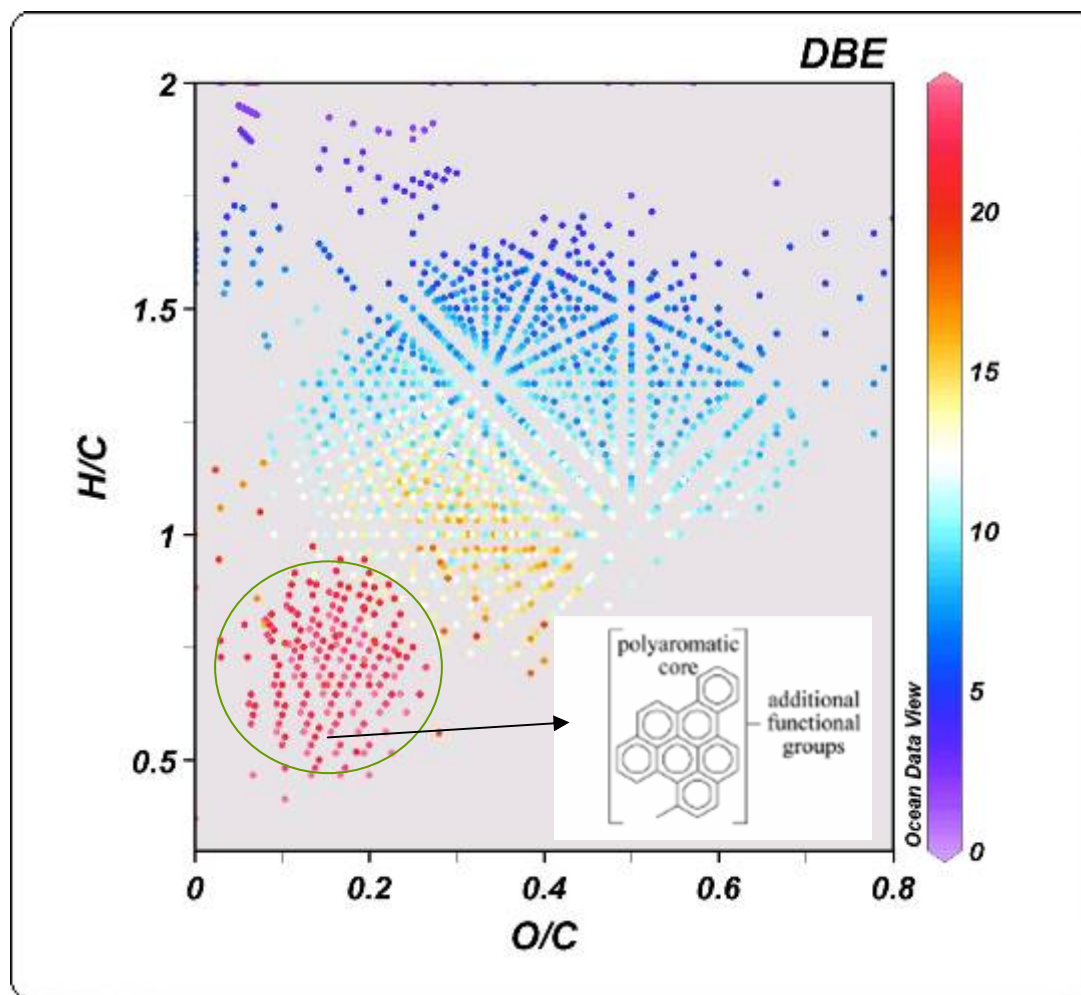


# Application 1: Offline-coupling to FT-ICR-MS



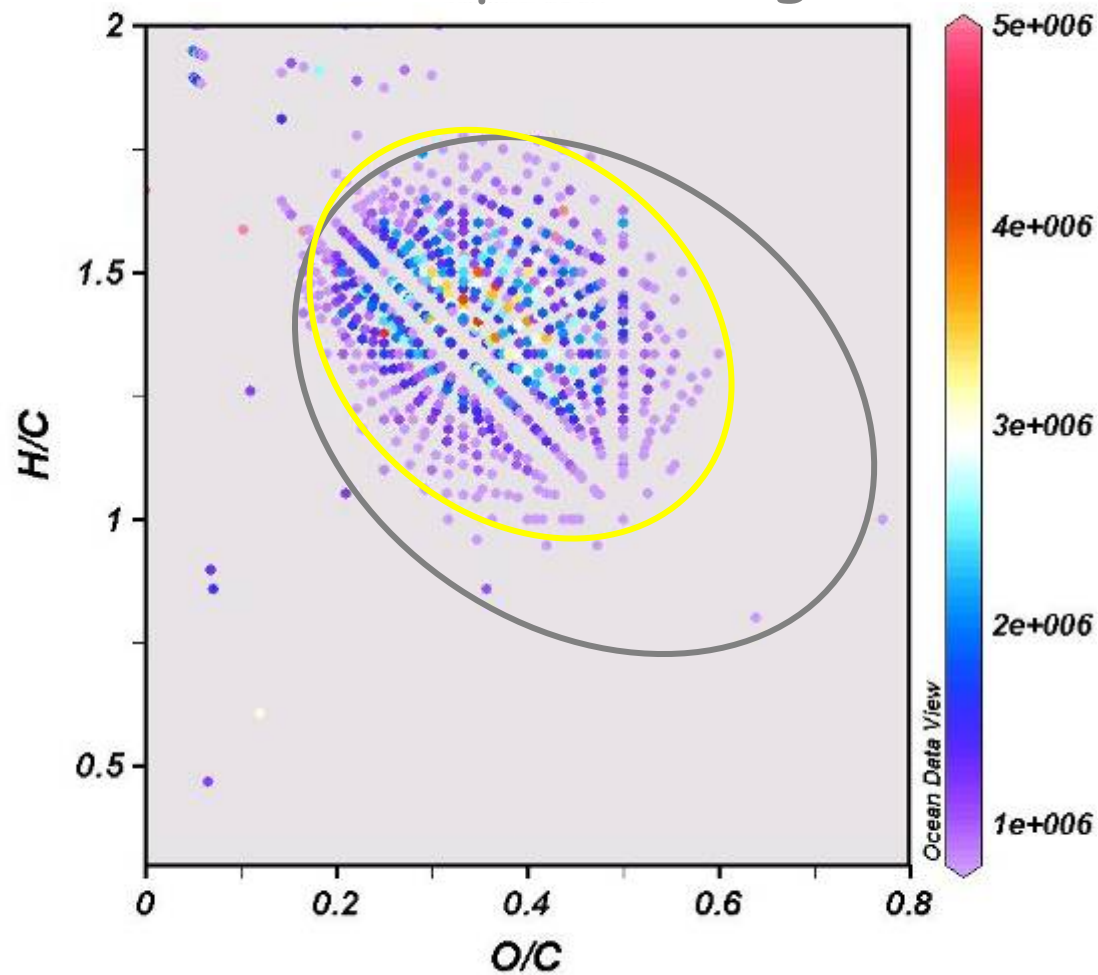
..... Intensity-weighted average, blank-corrected CHON<sub>1</sub> compounds, <600 m/z, ppm<0.5

## Marine bottom water





# Porewater, photo-degraded





# Detection

