Print version

CEE 697z
Organic Compounds in Water and Wastewater

NOM and MS Methods

Lecture #10

NOM Characterization

- Analytical Tests
  - elemental analysis
  - spectral properties
  - functional group chemistry
- Separation/Fractionation
  - resin adsorption
  - size exclusion chromatography
- Combinations

Practical Characterization of NOM

- Two necessary components
  - A set of useful, and accessible characterization tools (i.e., analytical methods)
  - A means by which NOM characteristics can be translated into information of practical importance (i.e., what does it all mean?)
- Progress is being made in both areas
  - NOM characterization is still more "scientific" that "practical"
    - exception: SUVA
  - However, NOM characterization will become far more important in the near future

Most Useful Characterization Methods

- Current, accessible methods
  - SUVA
  - Hydrophilic/hydrophobic
  - Absorbance at 272 nm???
- Future methods
  - HPLC & spectral based methods
  - Deconvolution of UV/Vis Spectrum
- Research methods (require expensive equipment)
  - Pyrolysis - GC/MS
  - ^{13}C-NMR
  - LC/MS

Pyrolysis GC/MS

- high temperature, rapid thermal decomposition
- followed by mass spectrometry for identification of pyrolysis byproducts
- difficult, and not quantitative, or at best, semi-quantatitive
- can attribute pyrolysis byproducts to starting structures

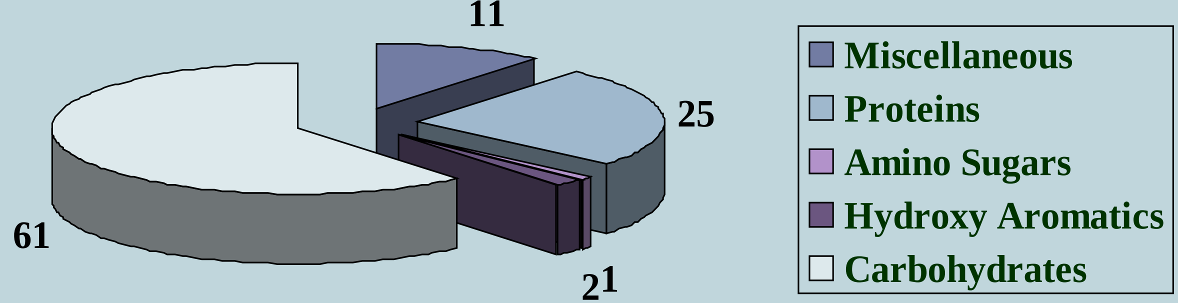
  .proteins (form pyrroles, indoles, phenol, p-cresol, nitriles)

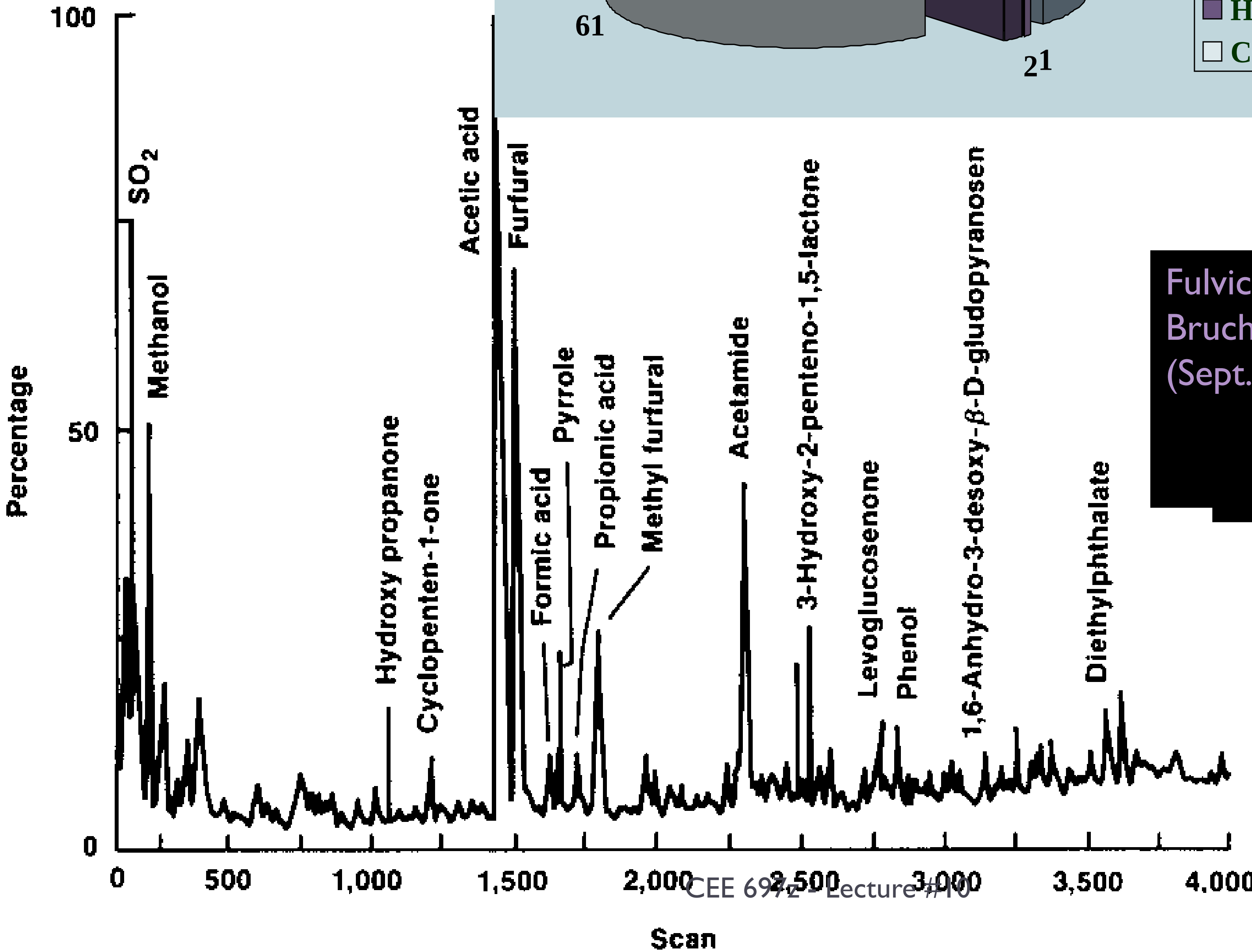
  .amino sugars (form acetamide)

  .polyhydroxy aromatics (various phenolic derivatives)

  .carbohydrates (form furans, acetic acid, and many carbonyl compounds) .carboxylic acids

- THMFP may be related to polyhydroxy aromatic content





Fulvic Acid from Bruchet et al., 1990 (Sept. J.AWWA)

HILIC - NMR

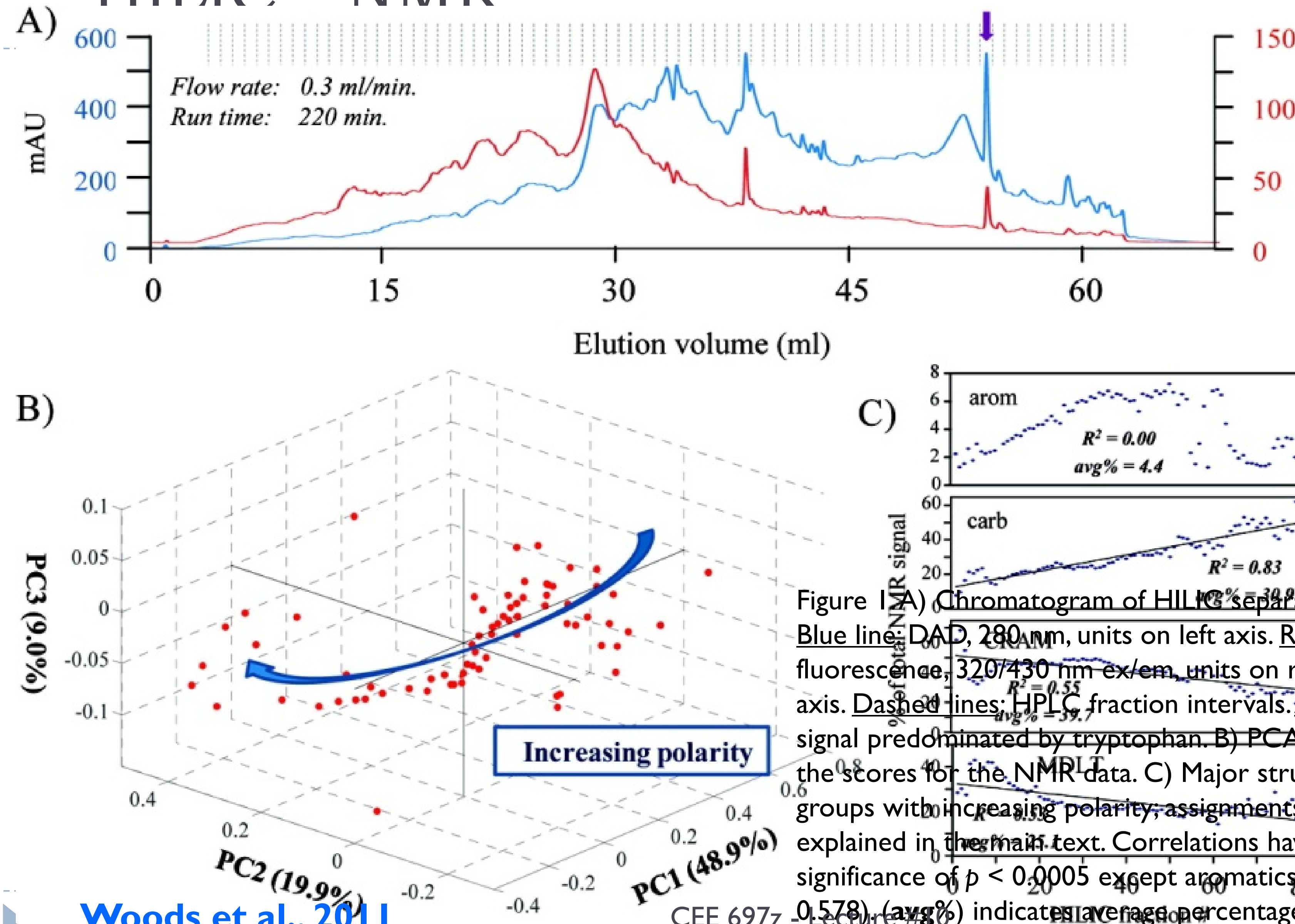
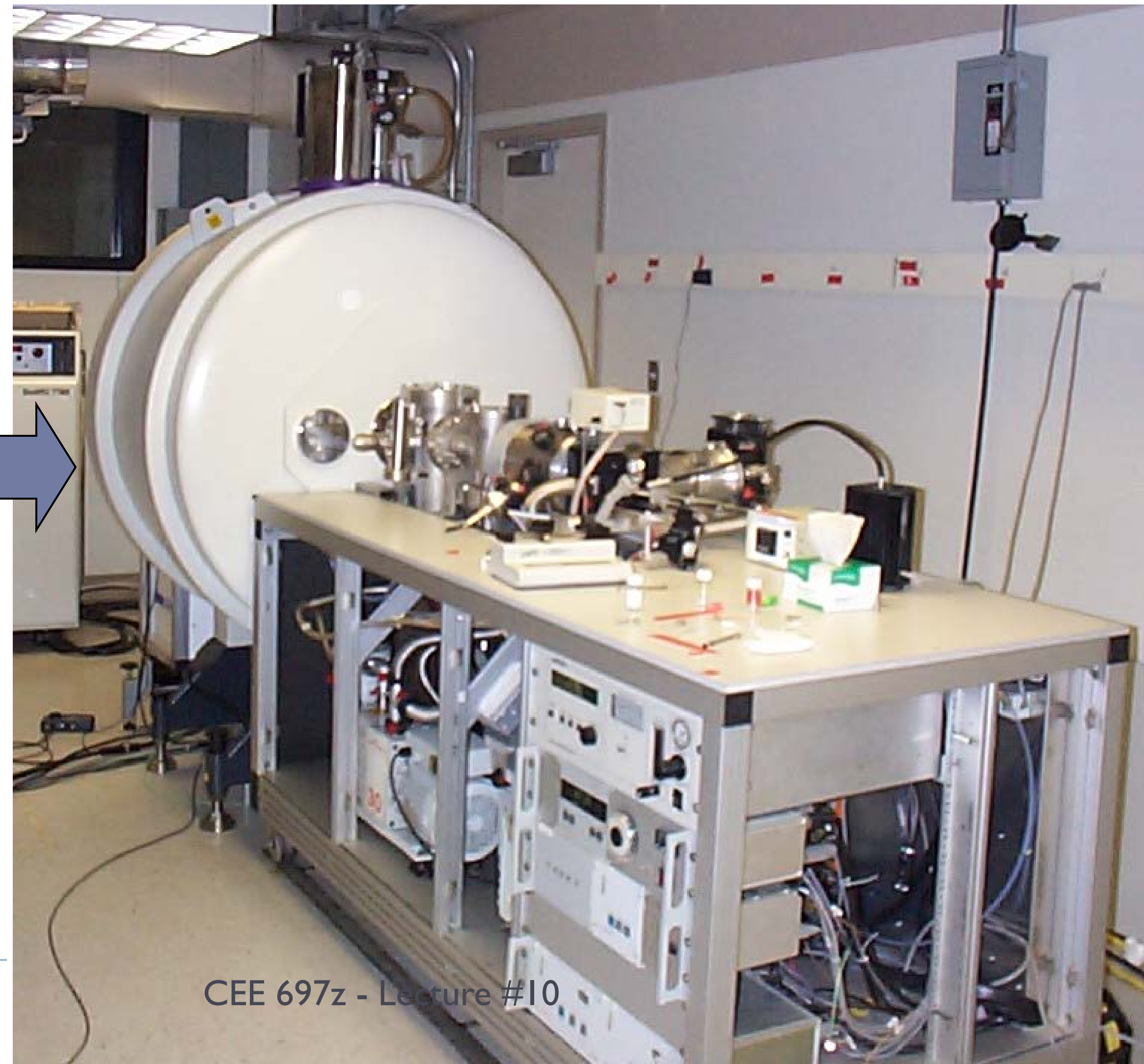


Figure 1 A) Chromatogram of HILIC separation. Blue line: DAD, 280 nm, units on left axis. Red line: fluorescence, 320/430 nm ex/em, units on right axis. Dashed lines: HPLC fraction intervals. Arrow: signal predominated by tryptophan. B) PCA plot of the scores for the NMR data. C) Major structural groups with increasing polarity; assignments explained in the main text. Correlations have a significance of $p < 0.0005$ except aromatics ($p = 0.578$). (avg%) indicates average percentage of NMR signal for all fractions

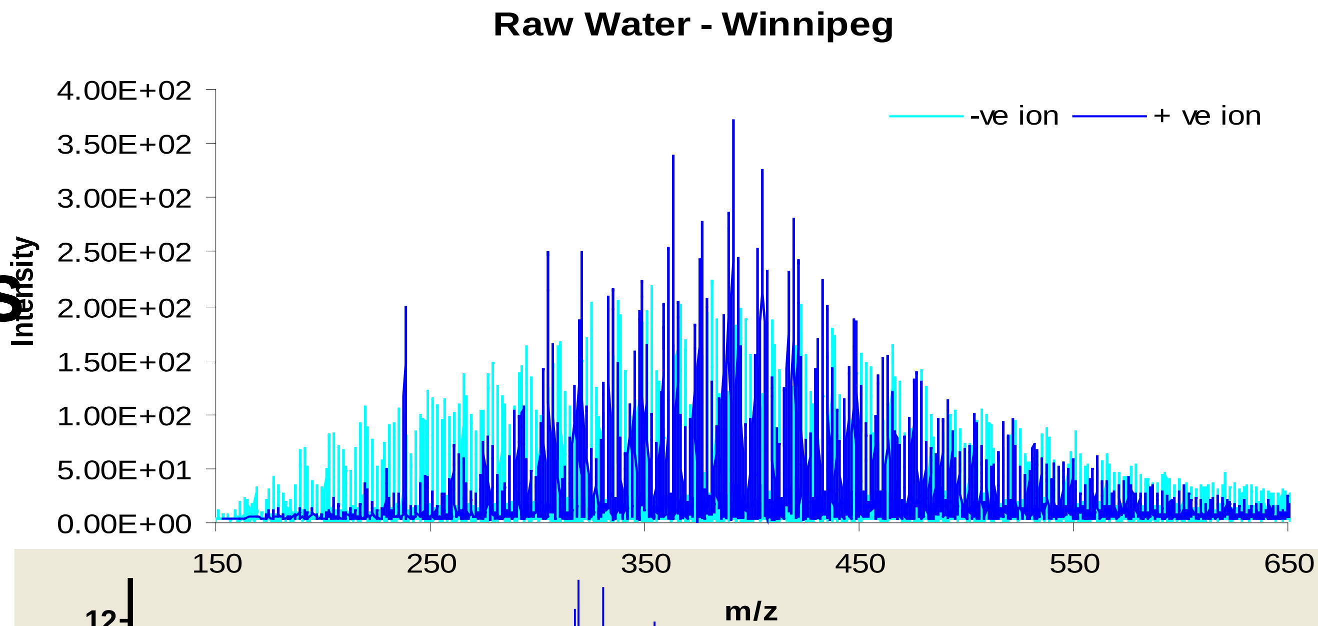
Woods et al., 2011

The Future??: Higher MW ID

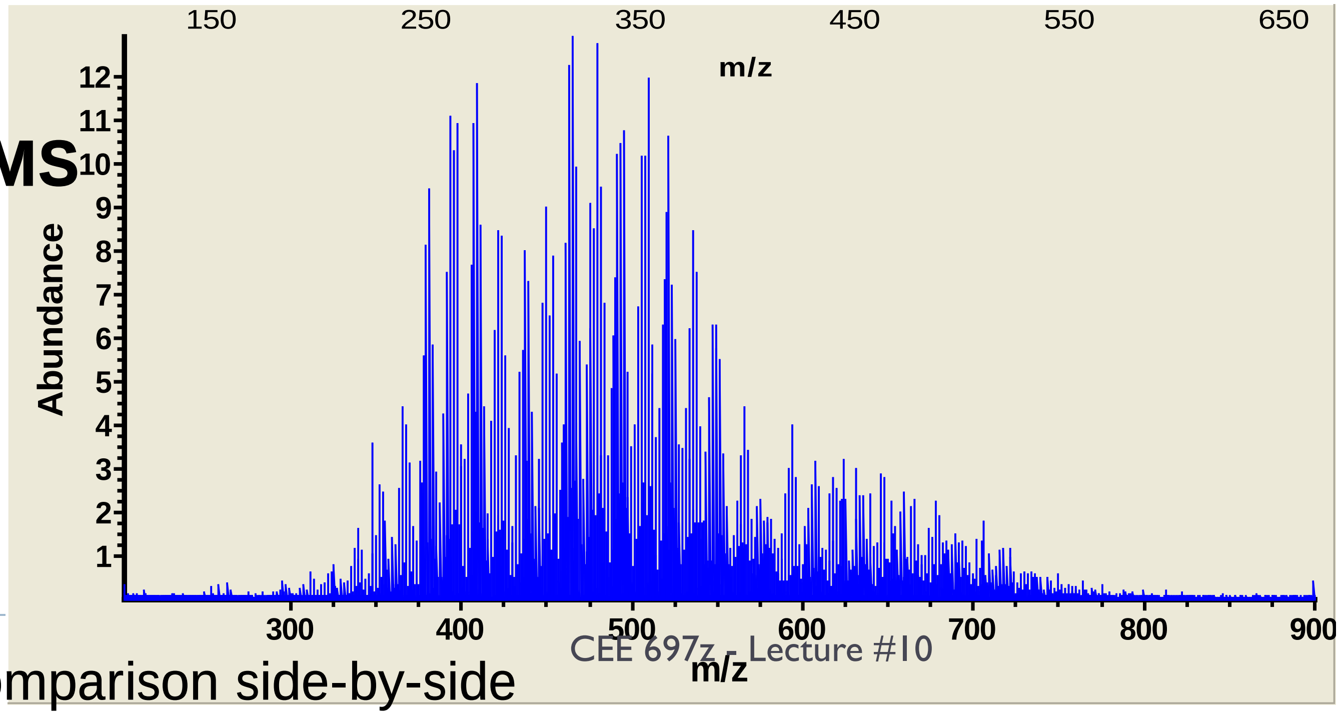
- NOM research
  - ESI with Ultra High-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Benefits
  - Unambiguous molecular formulae



ESI-TOF MS

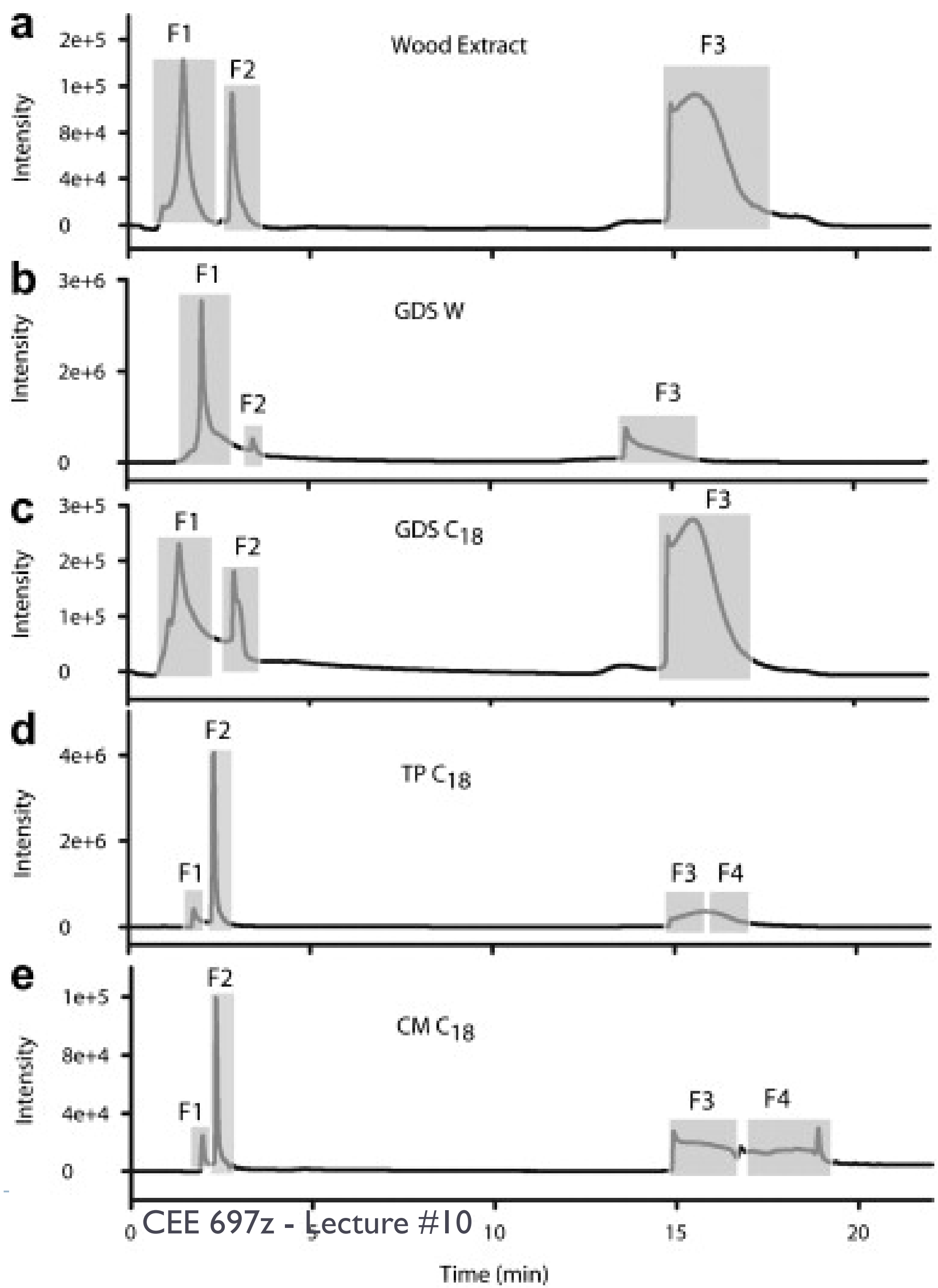


ESI-FTICR MS



- Same: comparison side-by-side

Fig. 2 HPLC chromatograms (UV at 254 nm) of a) wood extract; b) Great Dismal Swamp whole water (GDS W); c) C 18 extracted Great Dismal Swamp (GDS C 18) DOM; d) C 18 extracted Town Point (TP C 18) DOM; and e) C 18 extracted coastal marine (CM C 18) DO...

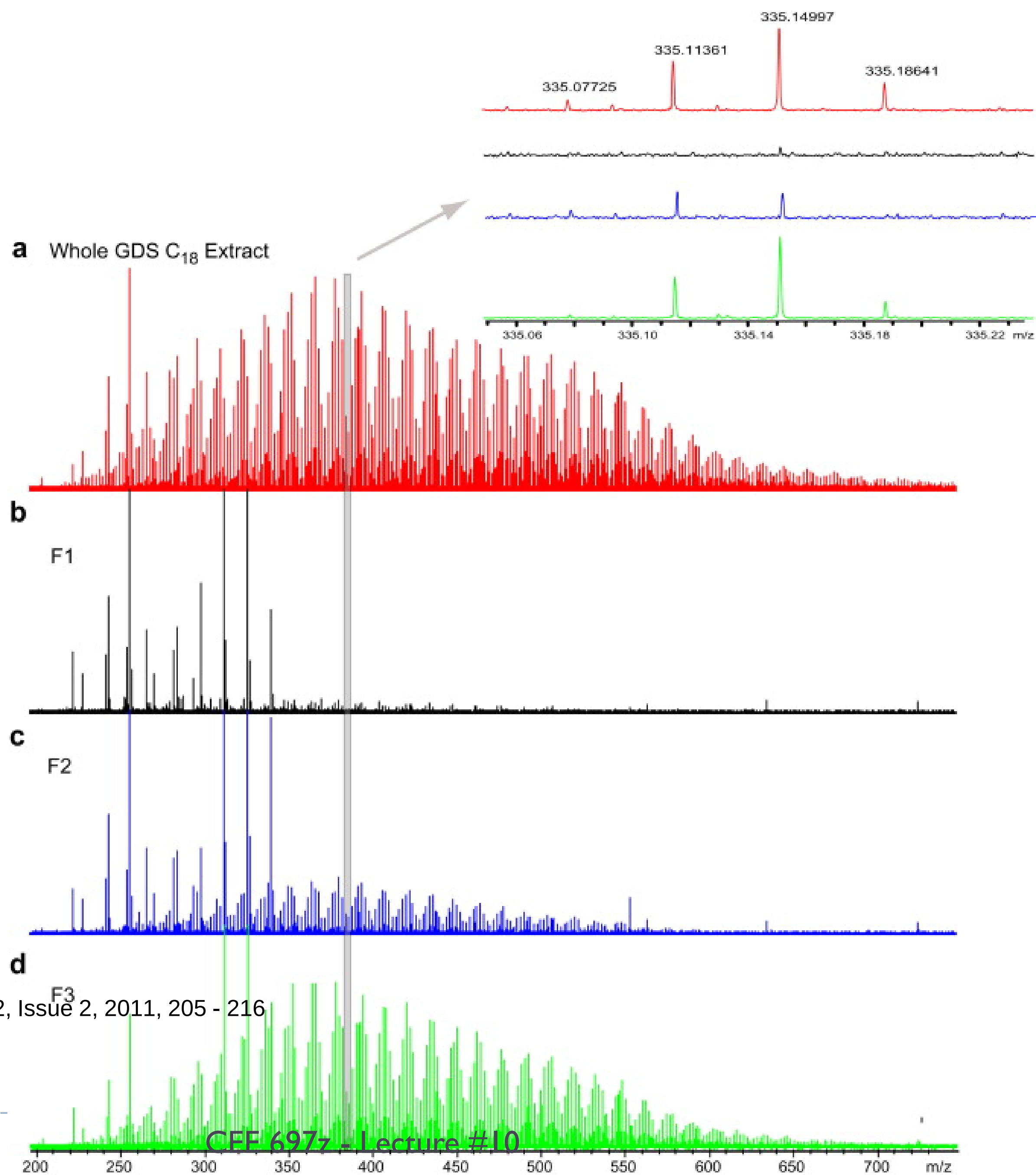


Zhanfei Liu , Rachel L. Sleighter ,
Junyan Zhong , Patrick G. Hatcher

The chemical changes of DOM from black waters to coastal marine waters by HPLC combined with ultrahigh resolution mass spectrometry

Estuarine, Coastal and Shelf Science,
Volume 92, Issue 2, 2011, 205 - 216

Fig. 3 FTICR mass spectra of the C 18 extracted Great Dismal Swamp DOM and its HPLC fractions (see <ce:cross-ref refid="fig2"> Fig. 2</ce:cross-ref> b for the corresponding HPLC collected fractions). The inset is an expanded region at nominal mass 335. Al...



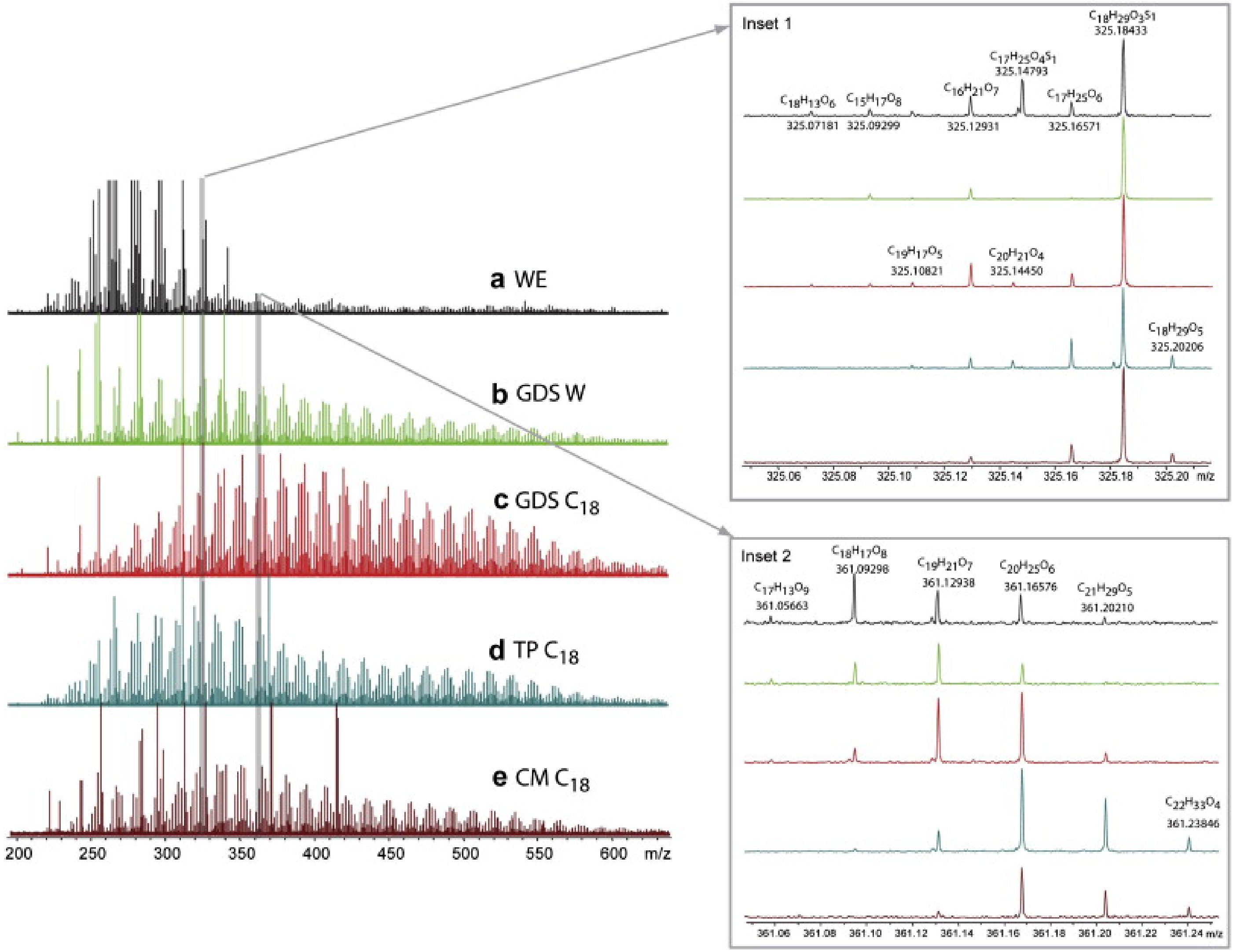
Zhanfei Liu , Rachel L. Sleighter , Junyan Zhong , Patrick G. Hatcher

The chemical changes of DOM from black waters to coastal marine waters by HPLC combined with ultrahigh resolution mass spectrometry

Estuarine, Coastal and Shelf Science, Volume 92, Issue 2, 2011, 205 - 216

http://dx.doi.org/10.1016/j.ecss.2010.12.030

Fig. 4 FTICR mass spectra of the HPLC hydrophobic fractions of the DOM samples. The spectra shown are fraction F3 from a) the wood extract (WE), b) Great Dismal Swamp whole water (GDS W), and c) C 18 extracted GDS DOM, as well as fraction F4 from C 18 ex...

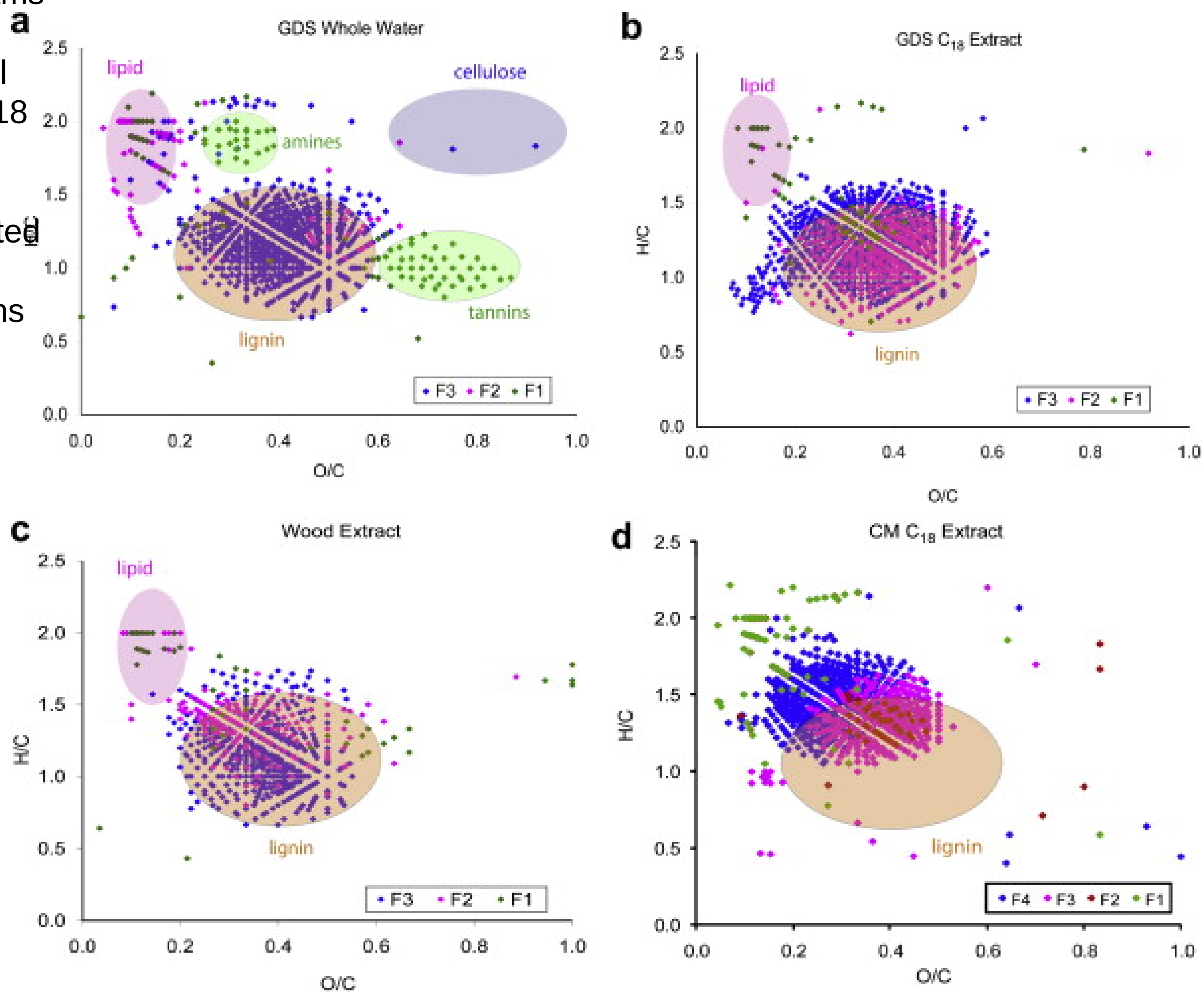


Zhanfei Liu , Rachel L. Sleighter , Junyan Zhong , Patrick G. Hatcher

The chemical changes of DOM from black waters to coastal marine waters by HPLC combined with ultrahigh resolution mass spectrometry

Estuarine, Coastal and Shelf Science, Volume 92, Issue 2, 2011, 205 - 216

Fig. 5 van Krevelen diagrams of the collected HPLC fractions of a) Great Dismal Swamp whole water; b) C 18 extracted Great Dismal Swamp DOM, c) the wood extract, and d) C 18 extracted coastal marine DOM. The details of the HPLC fractions (F1-F3) are prov...

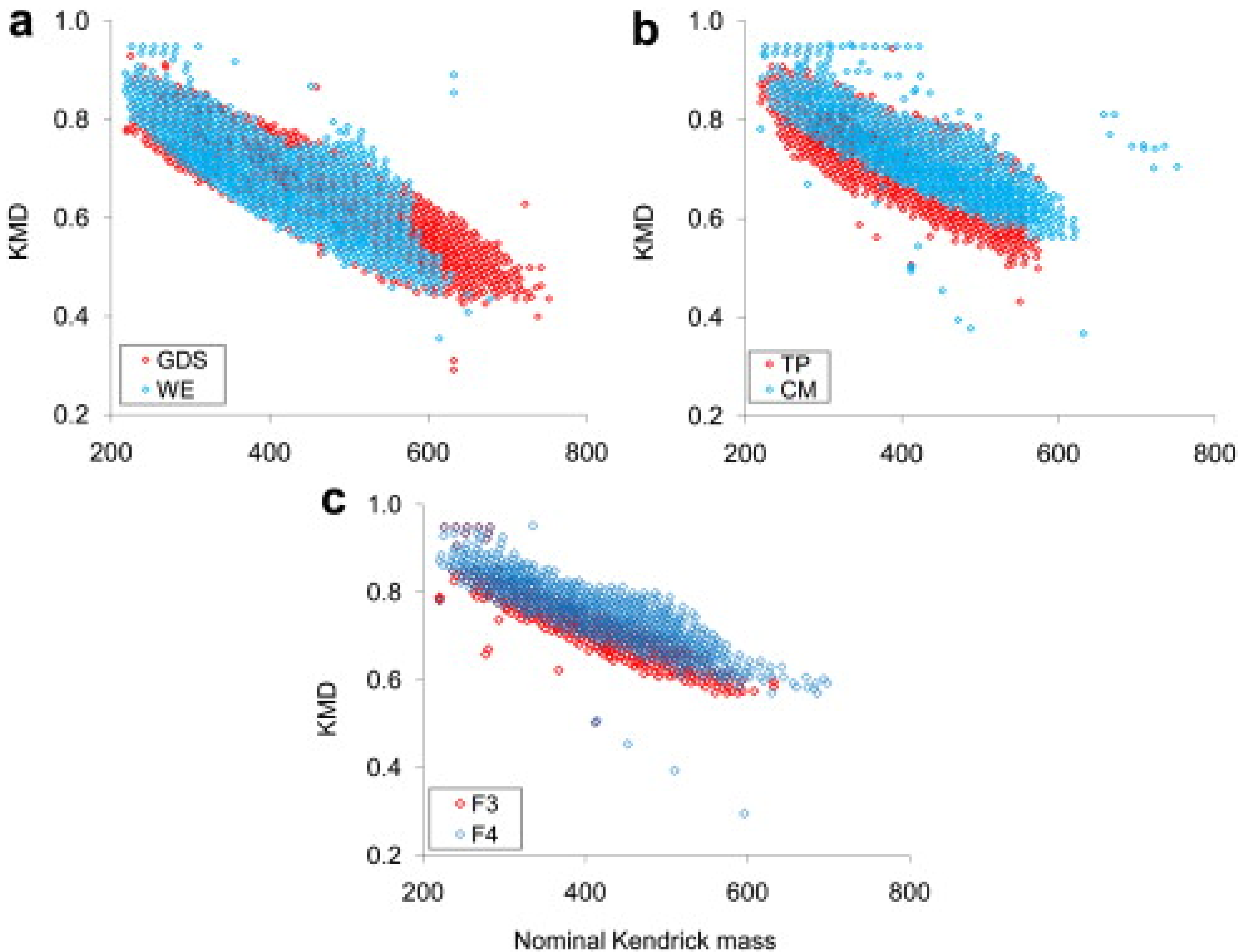


Zhanfei Liu , Rachel L. Sleighter , Junyan Zhong , Patrick G. Hatcher

The chemical changes of DOM from black waters to coastal marine waters by HPLC combined with ultrahigh resolution mass spectrometry

Estuarine, Coastal and Shelf Science, Volume 92, Issue 2, 2011, 205 - 216

Fig. 6 Kendrick mass defect plots of DOM from a) wood extract (WE) and C 18 extracted GDS water (GDS); b) C 18 extracted TP and CM water; and c) HPLC fraction F3 and F4 of C 18 extracted CM water.

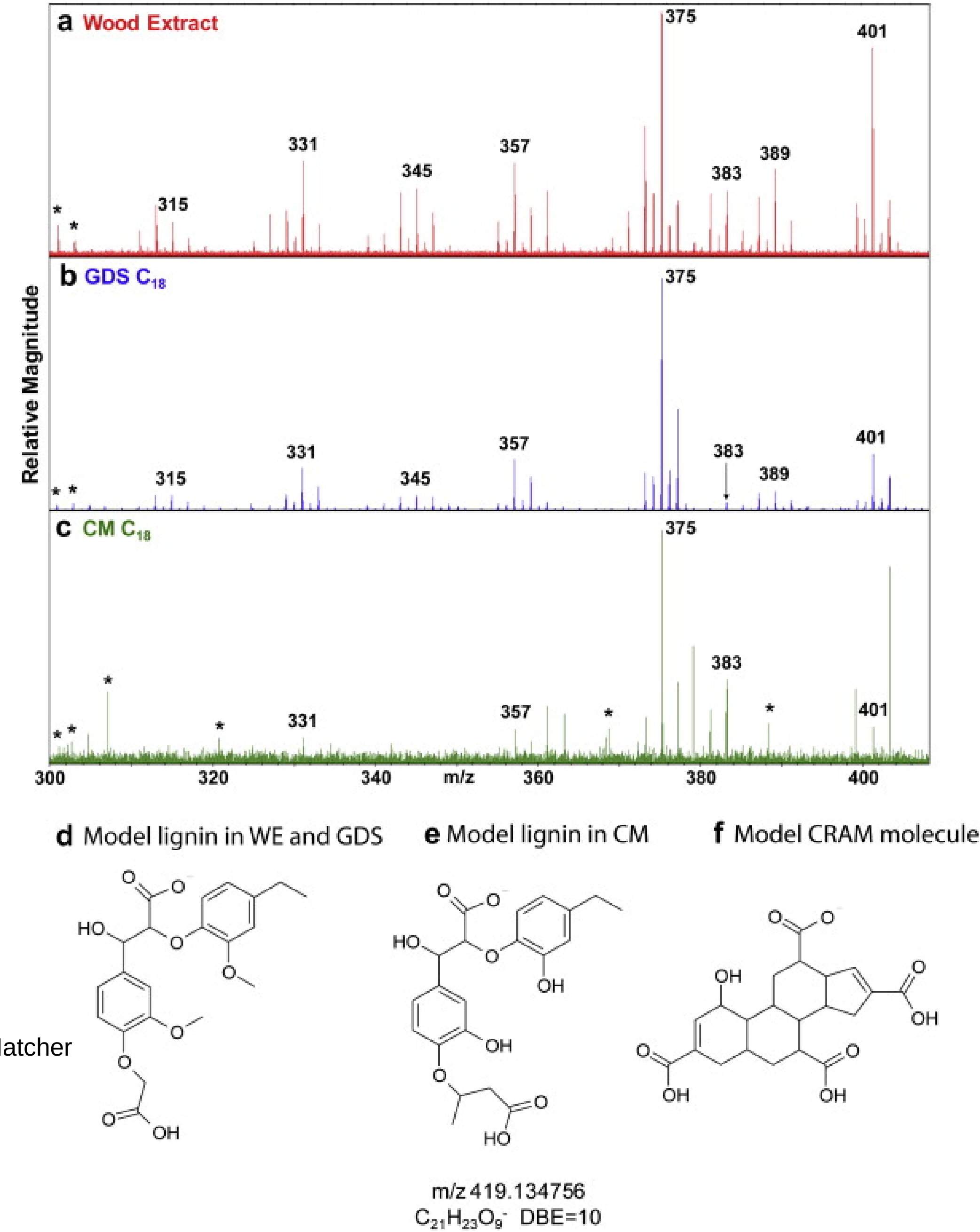


Zhanfei Liu , Rachel L. Sleighter , Junyan Zhong , Patrick G. Hatcher

The chemical changes of DOM from black waters to coastal marine waters by HPLC combined with ultrahigh resolution mass spectrometry

Estuarine, Coastal and Shelf Science, Volume 92, Issue 2, 2011, 205 - 216

Fig. 8 FTICR mass spectra of the CID fragmentation of nominal mass 419 of the a) wood extract (red); b) C 18 extracted GDS DOM (blue); and c) C 18 extracted CM DOM (green). Asterisks (∗) indicate noise peaks, rather than fragments. The possible structure...



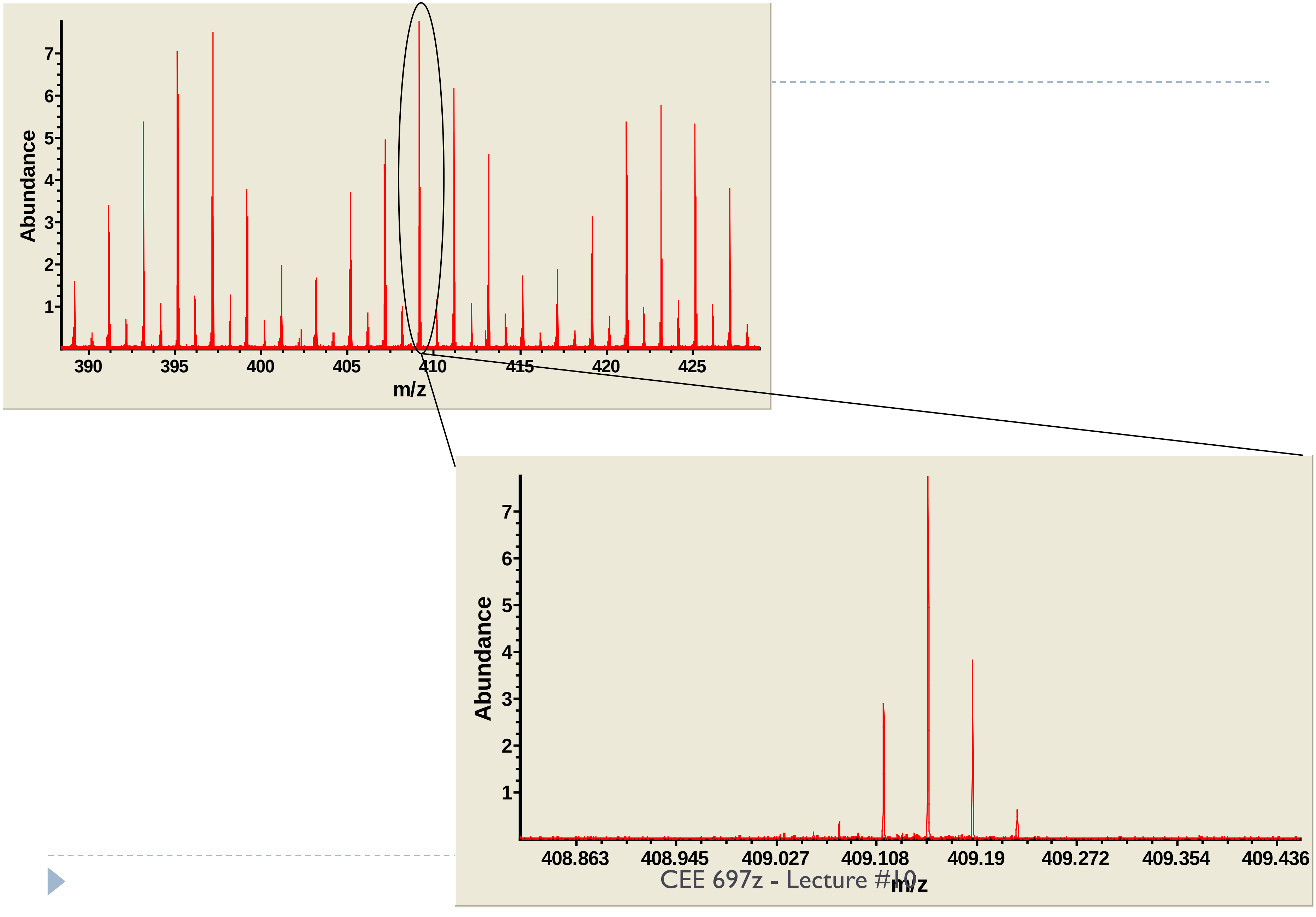
CRAM = Carboxyl Rich Alicyclic Molecules

Zhanfei Liu , Rachel L. Sleighter , Junyan Zhong , Patrick G. Hatcher

The chemical changes of DOM from black waters to coastal marine waters by HPLC combined with ultrahigh resolution mass spectrometry

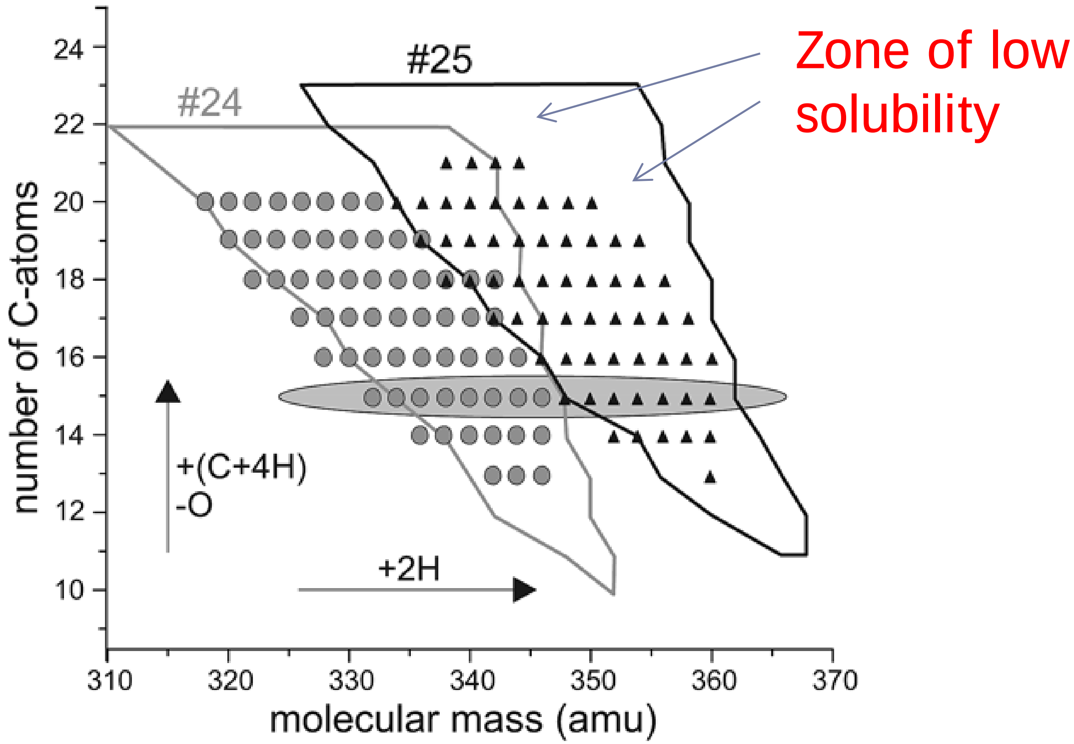
Estuarine, Coastal and Shelf Science, Volume 92, Issue 2, 2011, 205 - 216

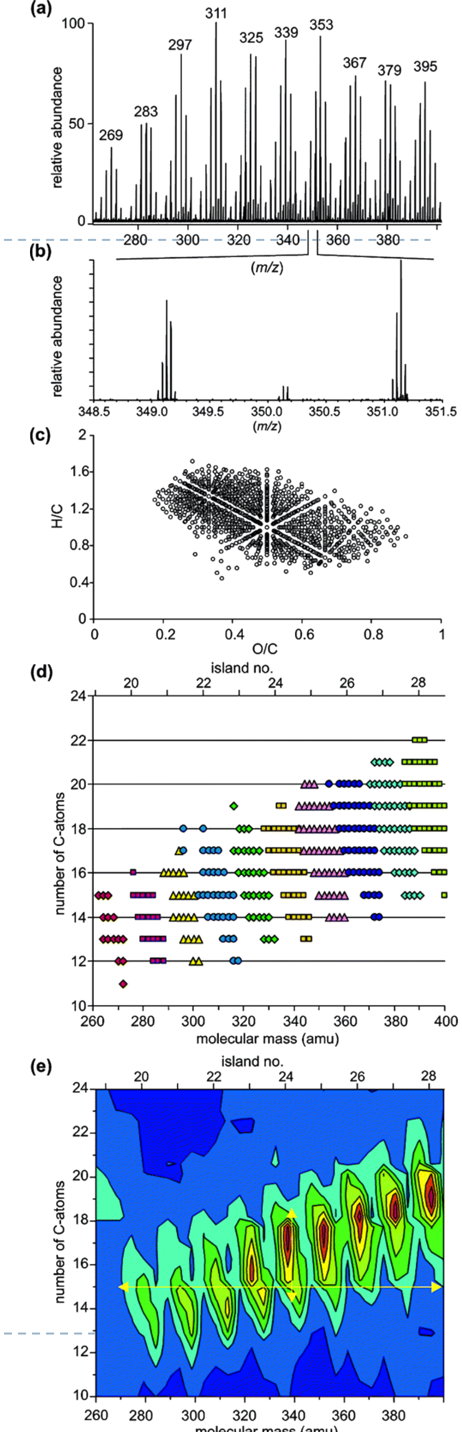
Chlorinated Water + Br Winnipeg



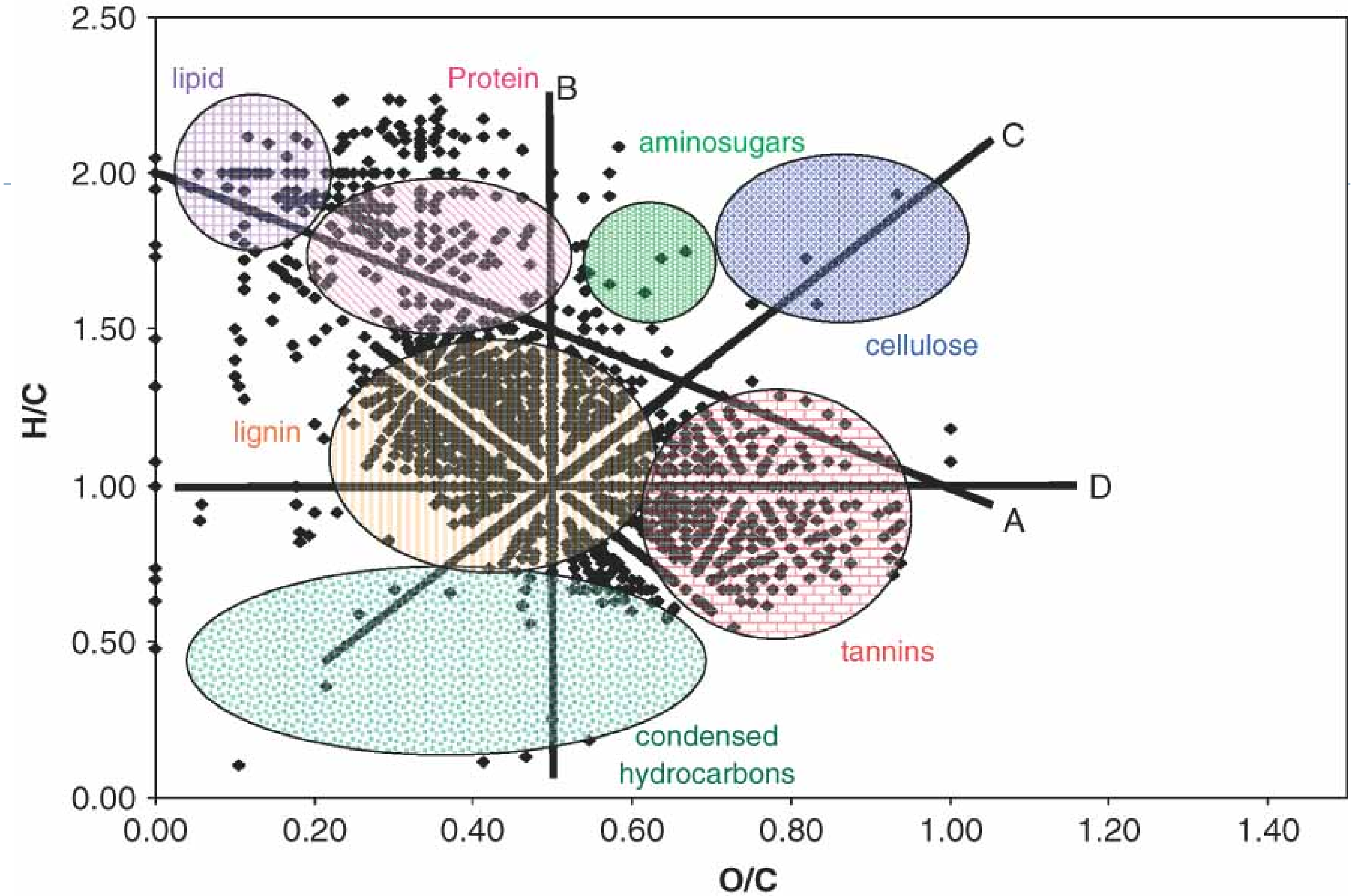
Ultra-high resolution MS

Reemtsma et al., 2006 [ES&T: 40:19:5839]





Area of predicted fulvic acid molecules in a C- vs molecular mass diagram for the mass range *m/z* 310-370 (marked by the lines) and fulvic acid molecules detected by SEC-FTICR-MS in the river isolate (dots (island no. 24) and triangles (island no. 25)).



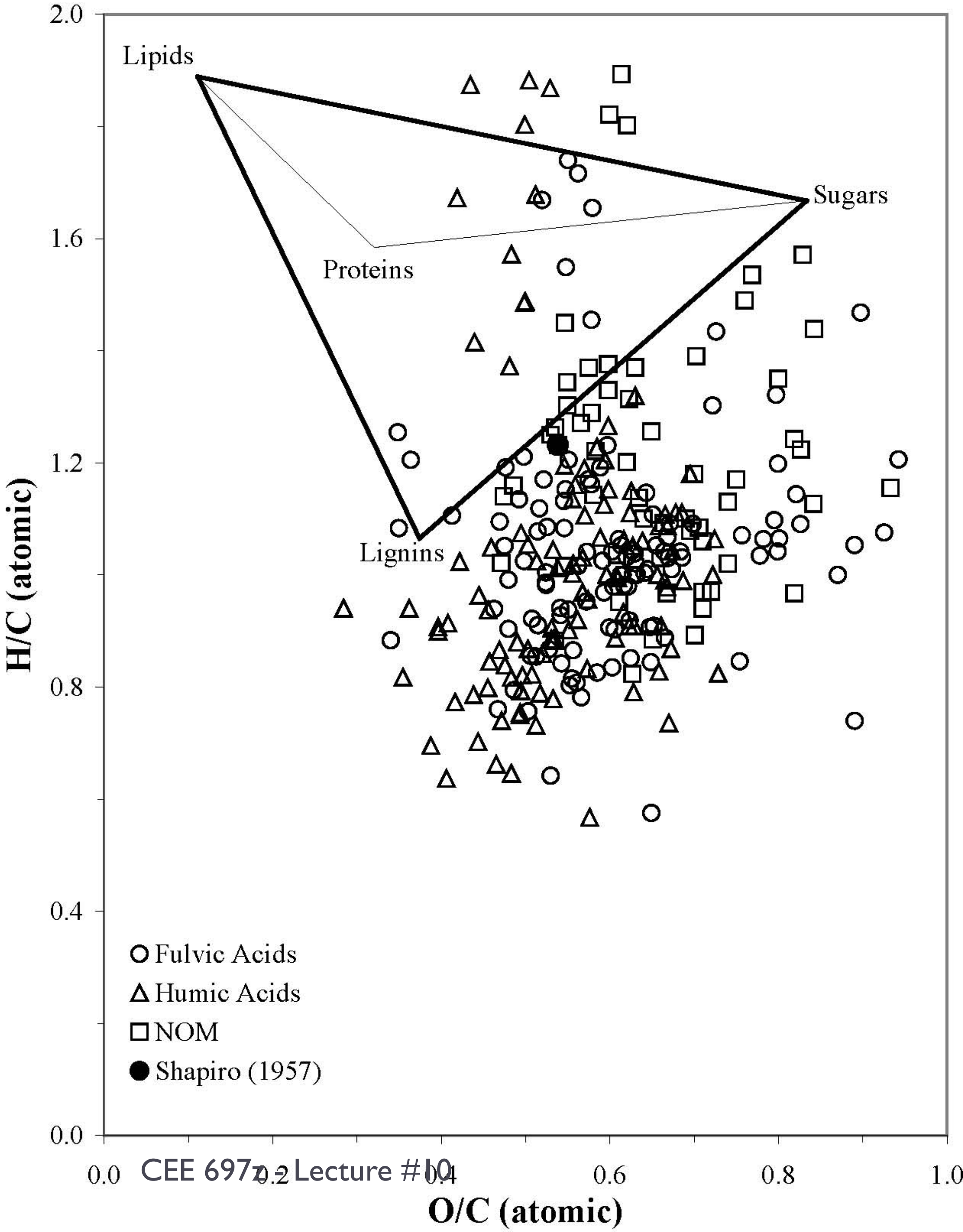
- Van Krevelen diagram for the Dismal Swamp DOM, compound classes are represented by the circles overlain on the plot. The distinctive lines in the plot denote the following chemical reactions: (A) methylation/demethylation, or alkyl chain elongation; (B) hydrogenation/dehydrogenation; (C) hydration/condensation; and (D) oxidation/reduction.

Sleighter & Hatcher, 2007 [J. Mass Spec. 42:559]

Elemental Ratios

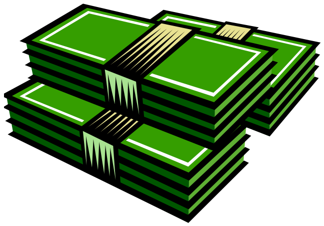
- Van Krevelen Plot

From:
Perdue & Ritchie, 2004

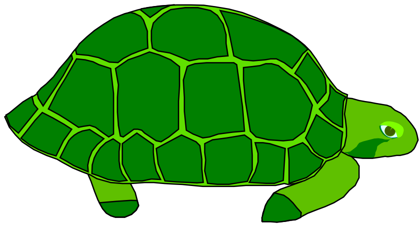


How to measure NOM

- Identify and quantify individual compounds
  - expensive and may only account for 10%
  - not practical



- Fractionate, extract and weigh
  - comprehensive, but time-consuming
  - doesn't tell us precisely what the stuff is



- Use a collective or "gross" measurement
  - TOC, UV absorbance, DBP precursors
  - easiest method, useful for engineering purposes

NOM Characterization

- Analytical Tests
  - elemental analysis
  - spectral properties
  - functional group chemistry
- Separation/Fractionation
  - resin adsorption
  - size exclusion chromatography
- Combinations

Adapted from Kornegay et al., 2000

NOM Characterization

Composition

- Elemental Analysis
  - TOC/DOC
  - TKN or TN
  - TOD or COD
  - CHON analysis
- Size
  - UF
  - Size Exclusion
  - FFF

Structural

- Absorbance
  - Color
  - UV abs
  - Fluorescence
- Acidity
- Hydrophobicity
- Pyrolysis-GC/MS
- FTIR
- NMR (^{13}C or H)
- LC/ESI-MS

Reactivity

- Disinfectant Reactivity
  - – THM/HAA FP
  - – Aldehyde formation
  - – Oxidant demand
- Coagulatability
- Biodegradability
  - – BDOC
  - – AOC

Light blue background signifies a "research method"

Summary and Conclusions

- Humic and Fulvic Acids
  - relatively hydrophobic, significant aromatic content, strong UV absorbance, moderate negative charge
  - they will be reactive with disinfectants, but easy to remove by coagulation
  - contain aromatic structures indicative of tannin and lignin residues
  - largely allochthonous

Summary (cont.)

- Non-humics
  - include hydrophilic acids, bases and neutrals and some hydrophobic materials
  - may be highly charged, or uncharged, lower MW, weak UV absorbance
  - they will be more soluble and difficult to remove by coagulation, but less reactive with disinfectants
  - many aliphatic structures indicative of a lipid hydrocarbon source
  - may be heavily autochthonous (algal derived)

Summary (cont.)

- DBP formation
  - most identified halogenated products result from free chloriation
  - concentrations of majors (THMs, HAAs) increase with reaction time, unless biodegradation occurs
  - pH and temperature play a significant role
  - bromide results in brominated forms of the DBPs
  - all disinfectants form oxygenated byproducts

- To next lecture