Print version

CEE 697z
Organic Compounds in Water and Wastewater

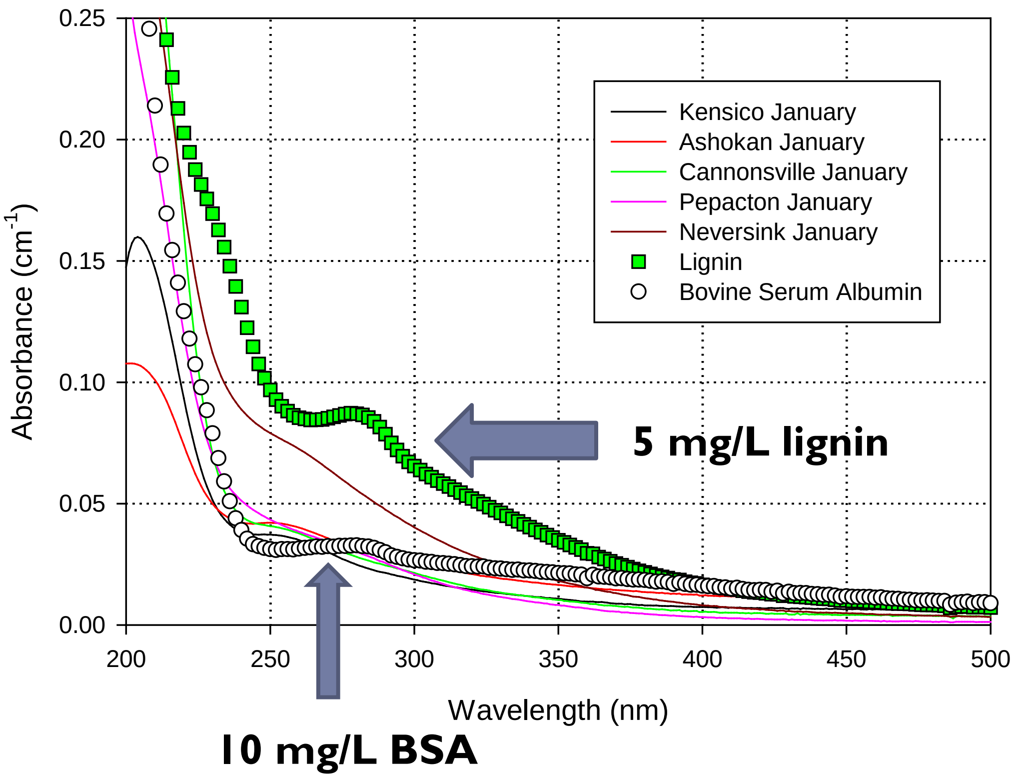
NOM Characterization II

Lecture #8

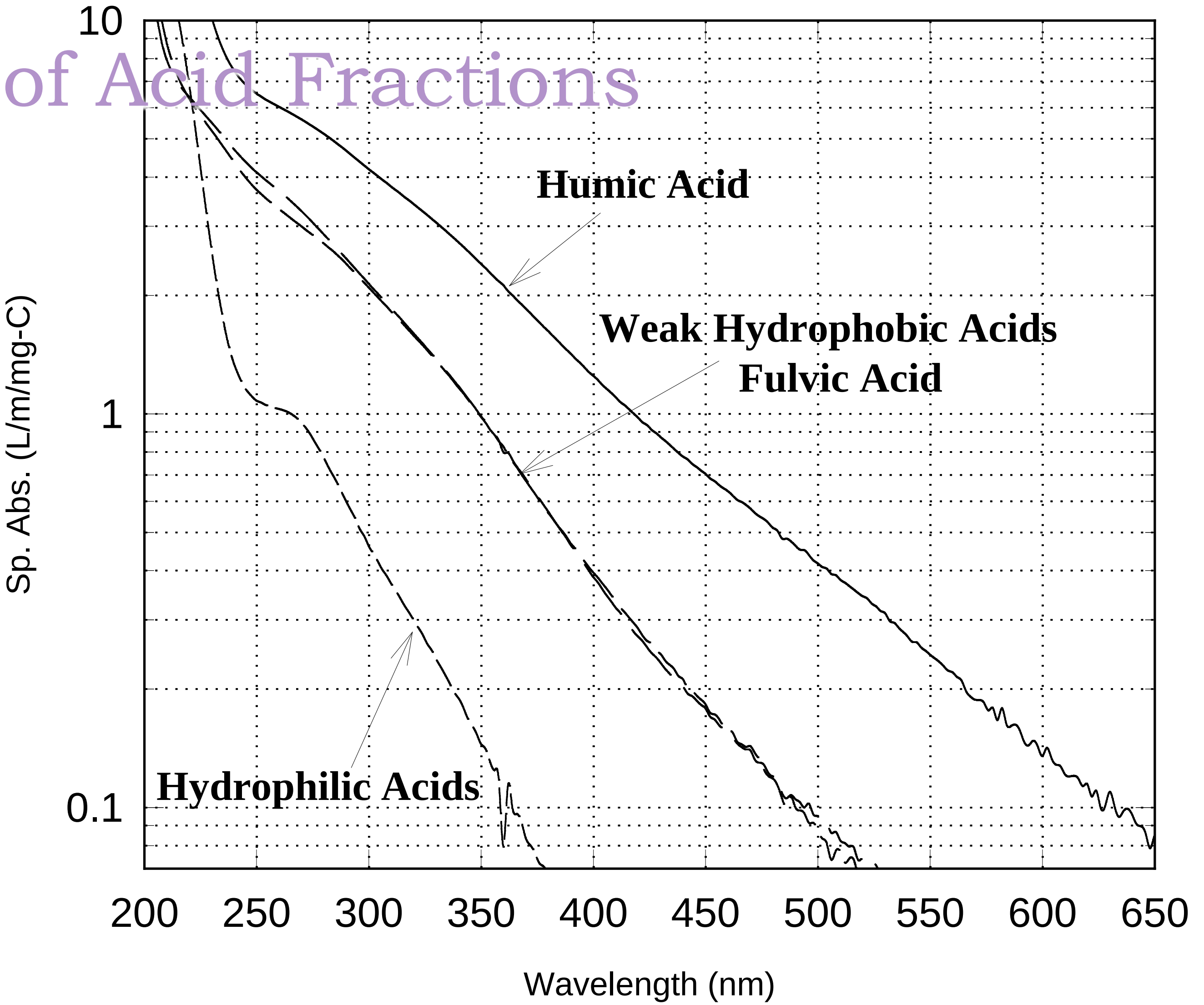
UV-Vis Absorbance Spectra

- Do we see "signatures of"
  - Proteins (Bovine Serum Albumin – a typical one)
  - Lignin

A 280 nm shoulder?

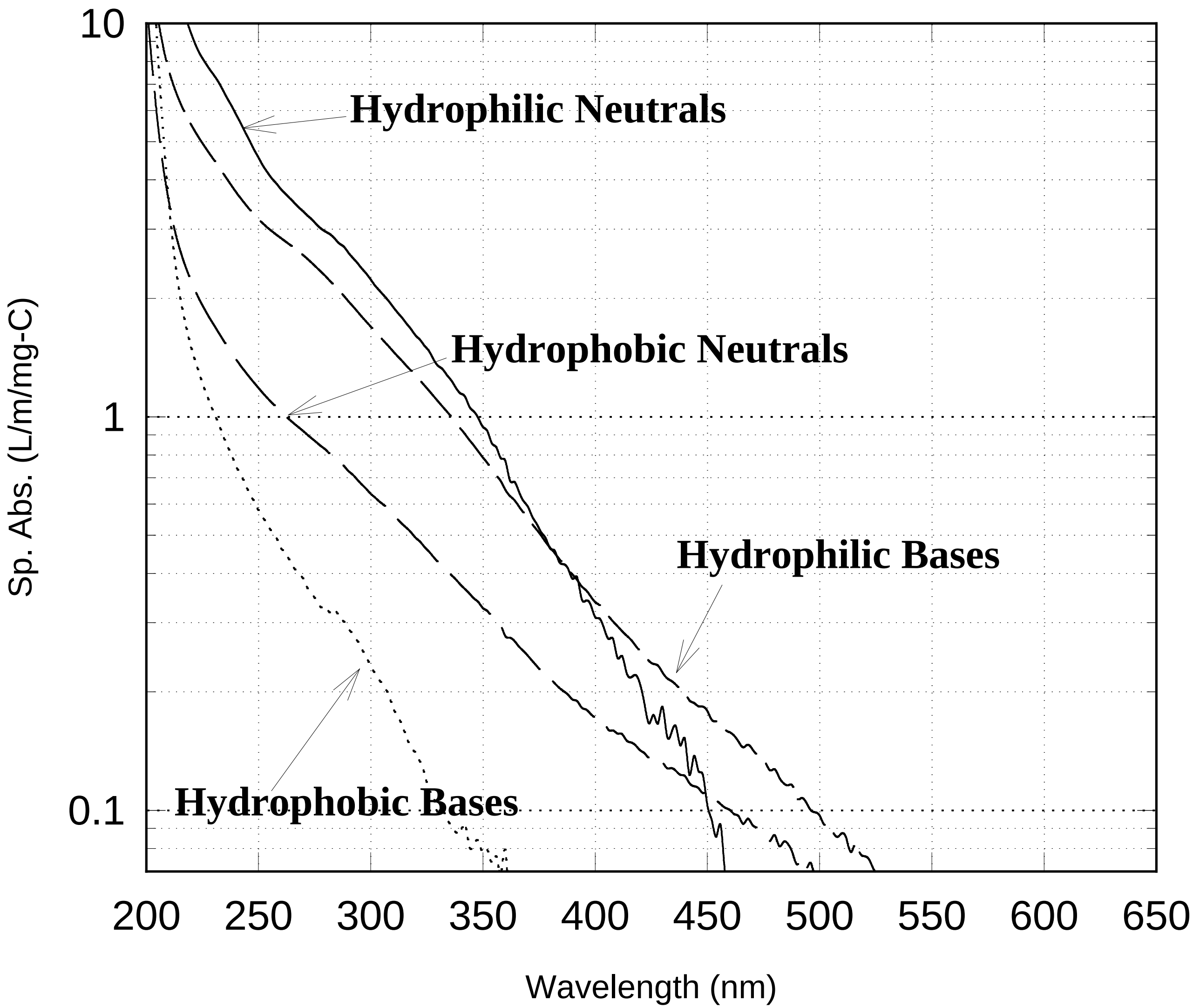


Absorbance of Acid Fractions



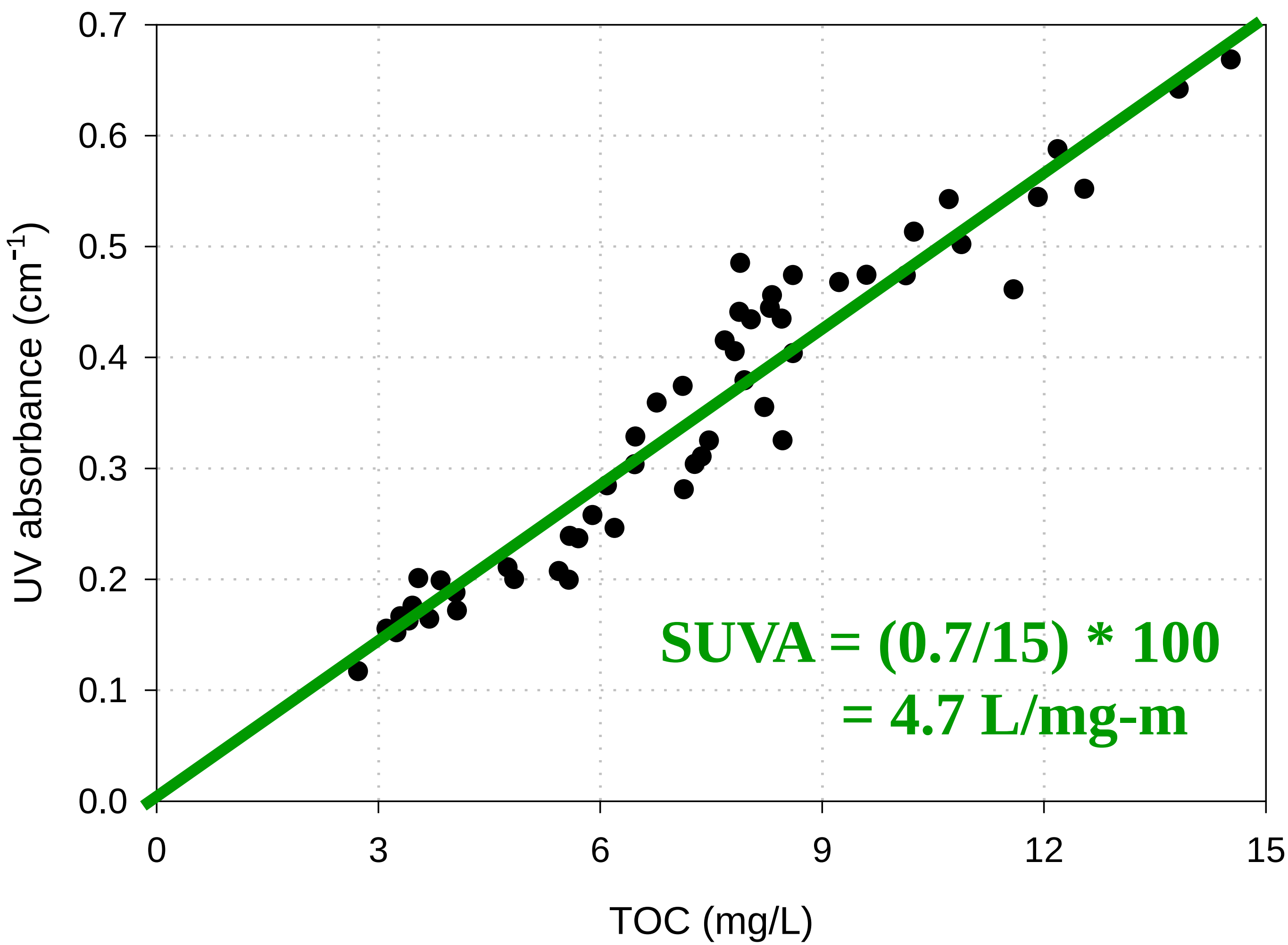
Same DOC

Absorbance of Bases & Neutrals



UV absorbance vs TOC: raw waters

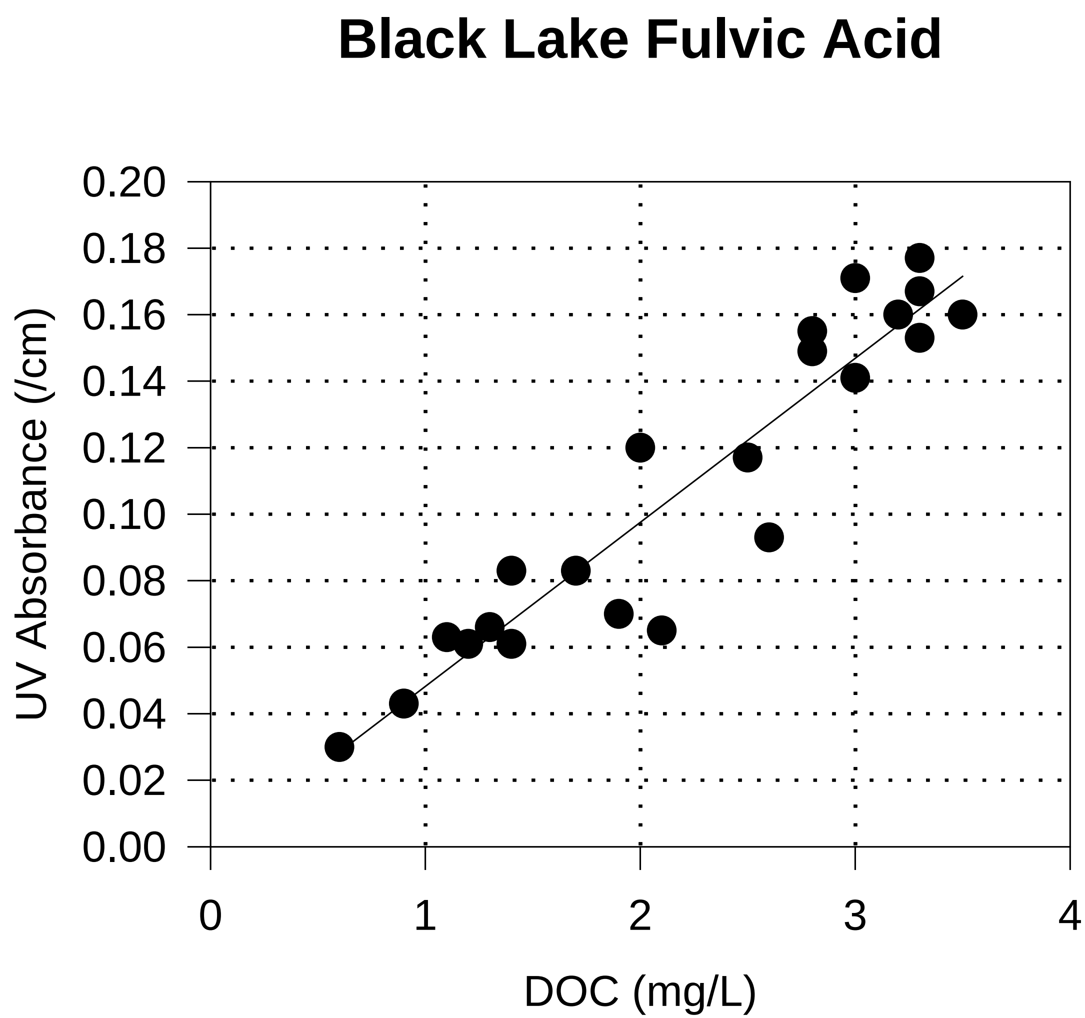
Correlation Between TOC and UV absorbance for 53 samples of Grasse River Water (from Edzwald et al., 1985)



UV absorbance vs DOC: treated waters

- surrogate for many organic parameters
- SUVA: specific UV absorbance, (UV/DOC)

Correlation Between DOC and UV absorbance for an Aquatic Fulvic Acid Subject to Coagulation at Various Alum Doses and various pHs (5-9) (from Reckhow, 1984)



Specific UV Absorbance (SUVA)

- UV absorbance at 254nm (cm^{-1}) divided by the DOC in mg/L (usually multiplied by 100)
- Relates to character of NOM
  - SUVA>4, water has a high humic character
    - high in hydrophobic organics, high MW, aromatic
  - SUVA=2-4, intermediate humic content
    - mix of hydrophobic and hydrophilic, medium MW
  - SUVA<2, mostly non-humic
    - hydrophilic organics, low MW, aliphatic

Some SUVA Values

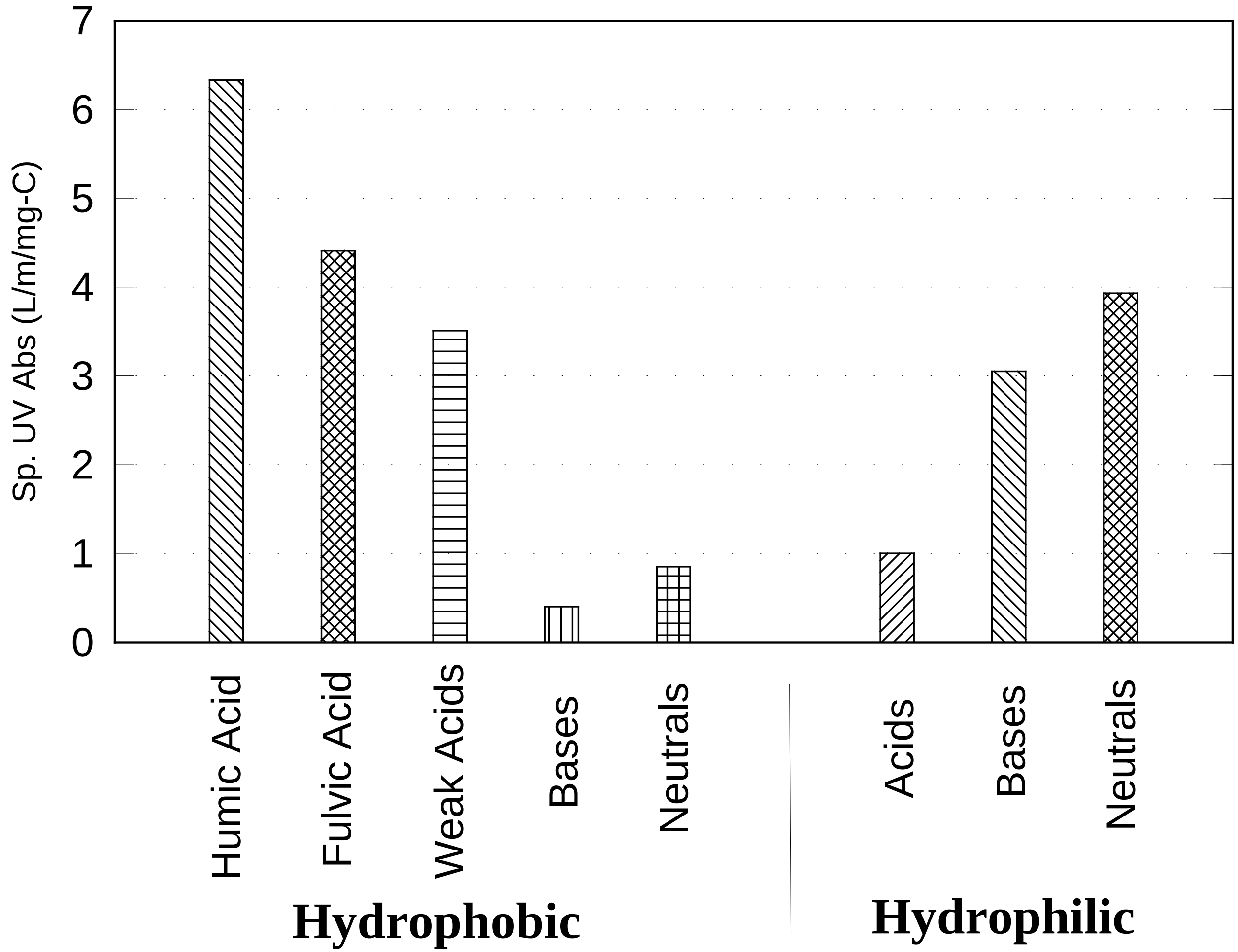
Source	SUVA (L/mg-m)
Typical HA	6
Typical FA	4
Lake Manatee, FL	5.7
Grasse River, NY	4.6
Mississippi, R., LA	3.1
Wachusett Res., MA	2.5
Quabbin Res., MA	1.8
Colorado R., CA	1.5

Aysgarth Falls, Yorkshire Dales

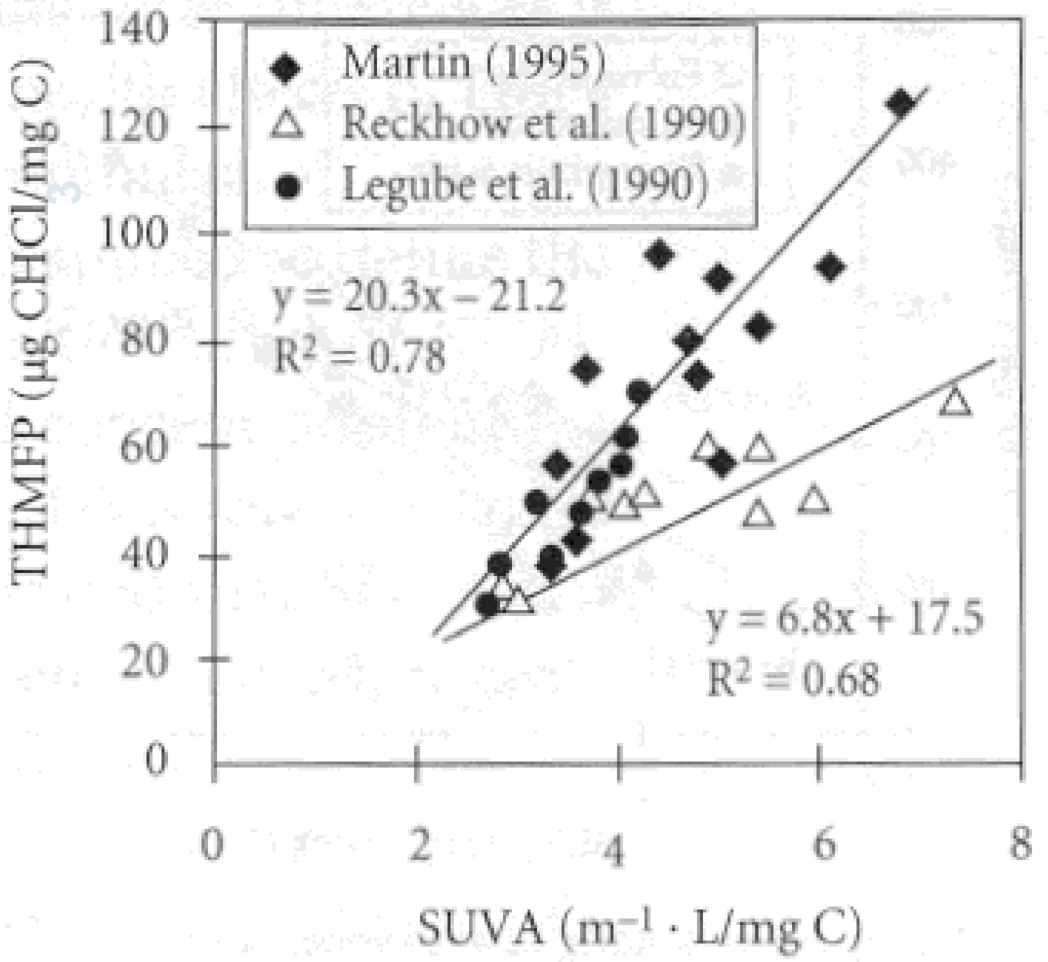
SUVA of NOM Fractions

Since treatment often results in preferential removal of humics, the SUVA in finished water is usually lower than in the raw water

Bleaching of NOM by chlorine makes this even more pronounced



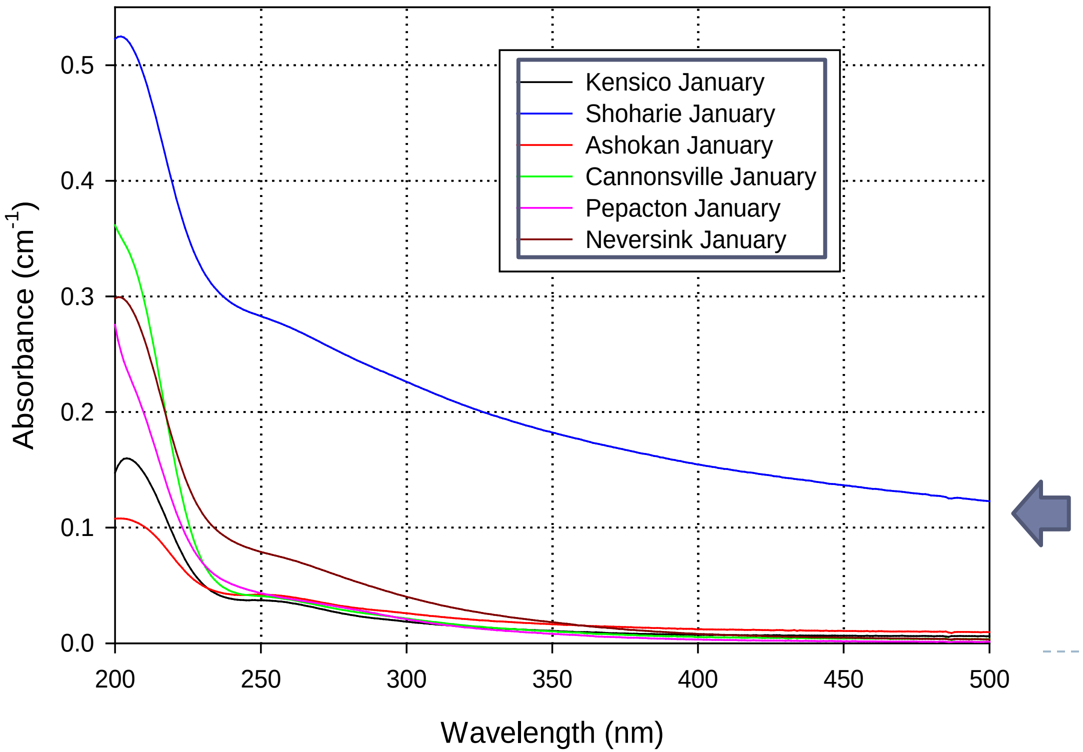
Surrogate Parameters/Correlations: (Normalized) THM Formation Potential (FP) versus SUVA (Croué)



from: Krasner & Amy

Bulk NOM Absorbance Spectra

- What information can we extract from this?
- Problem of particles

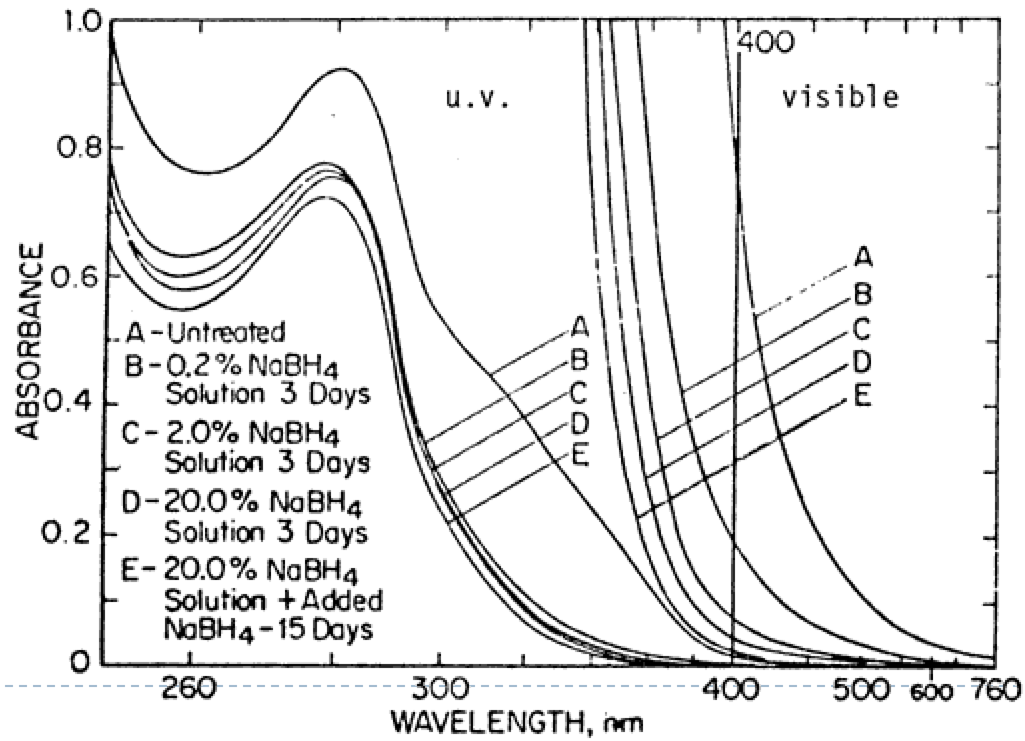


Problem with light scattering

Lignins

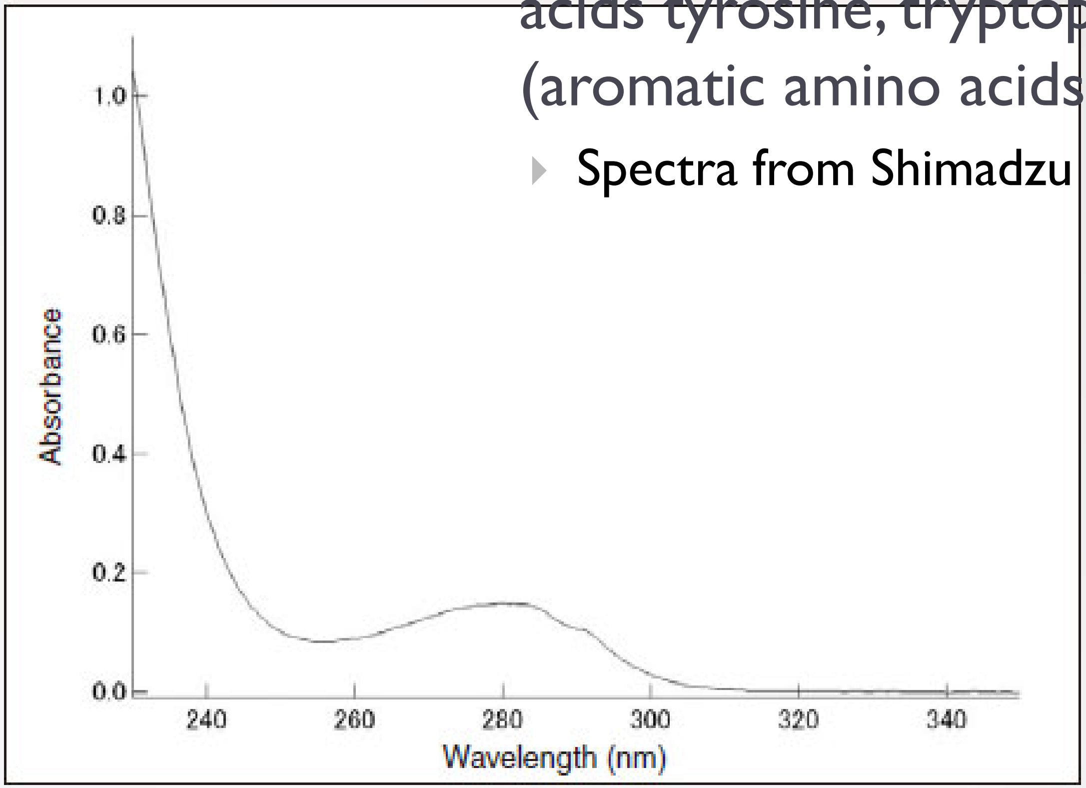
- Responsible for much of the tri-HAA?
- Absorbance spectra of Coniferous Lignin
  - Pew and Connors Tappi, 54 (1971), 245-251

Local Absorbance max at 280 nm



Proteins

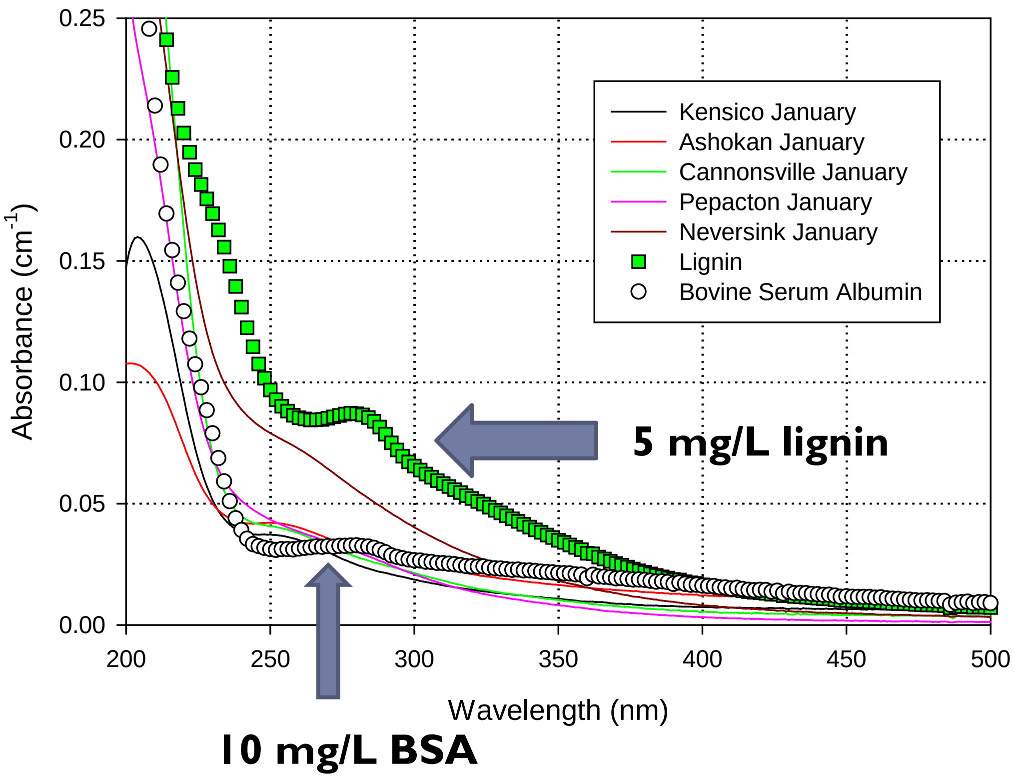
- Proteins generally exhibit a UVabs peak near 280 nm.
  - This absorption is due to the constituent amino acids tyrosine, tryptophan, and phenylalanine (aromatic amino acids).
    - Spectra from Shimadzu



Compare with NOM Spectra

- Do we see "signatures of"
  - Proteins (Bovine Serum Albumin – a typical one)
  - Lignin

A 280 nm shoulder?



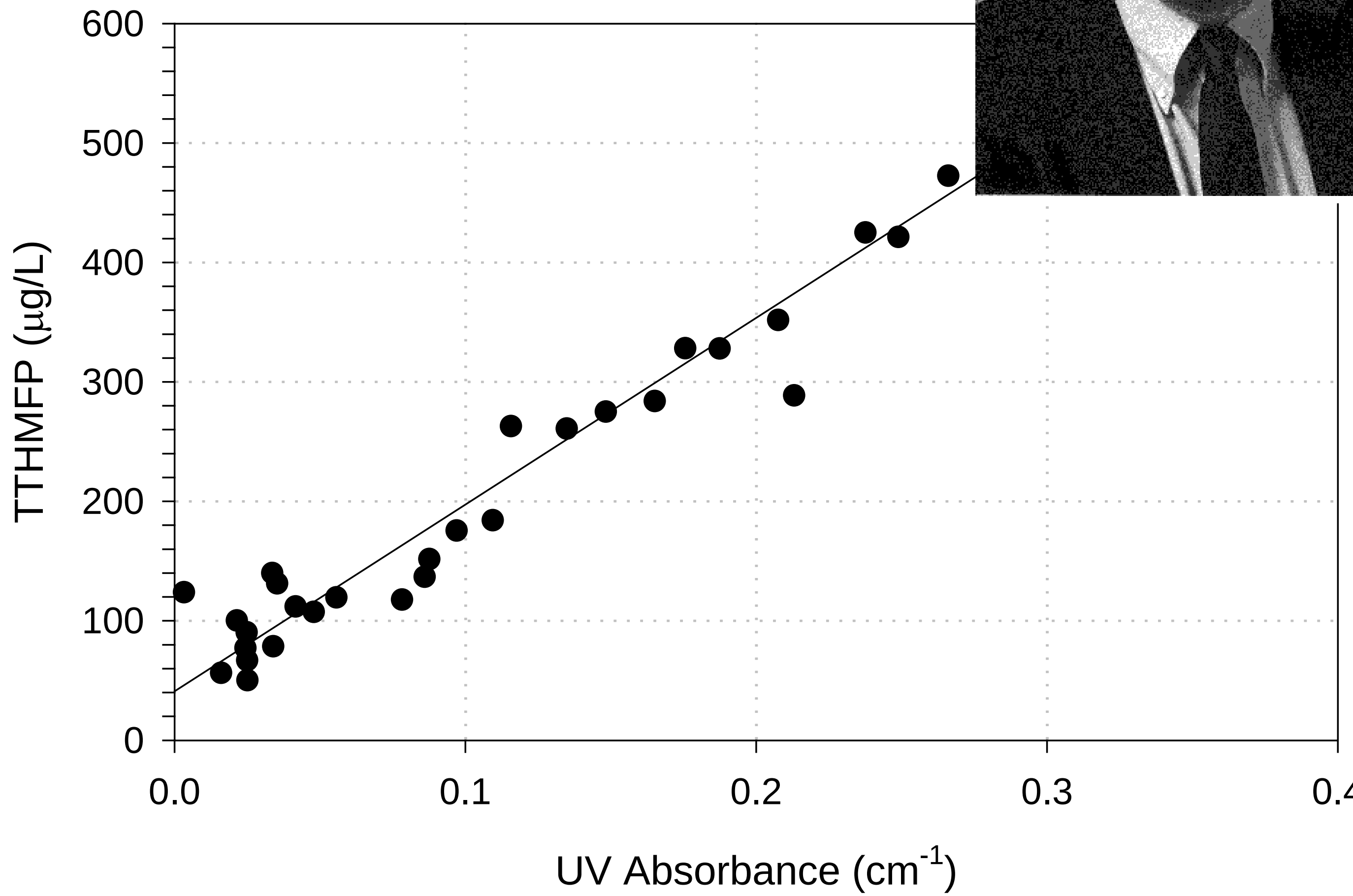
UV absorbance as a surrogate

- A good surrogate for DOC
  - especially when the character of the DOC is reasonably constant
- A very good surrogate for THMFP, HAAFP
  - takes into account reactivity of DOC as well as amount of DOC
- Oxidation processes (ozonation) disrupt relationships between UV and DOC or THMFP

Commercial field probe

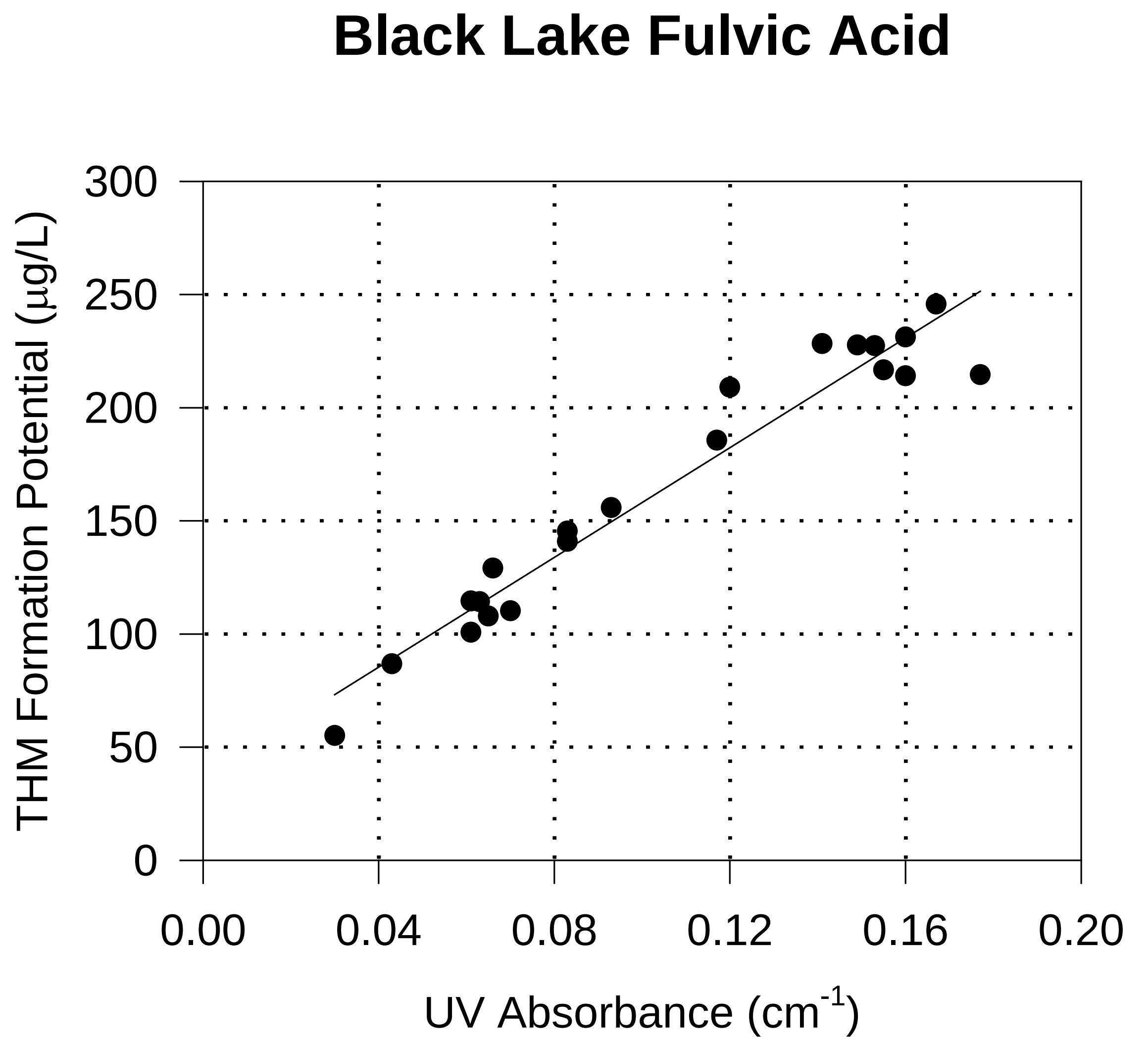
UV absorbance and THMFP

Correlation Between TTHMFP and UV absorbance for 31 samples of raw and treated water from the Oneida WTP (from Edzwald et al., 1985)



UV absorbance and THMFP

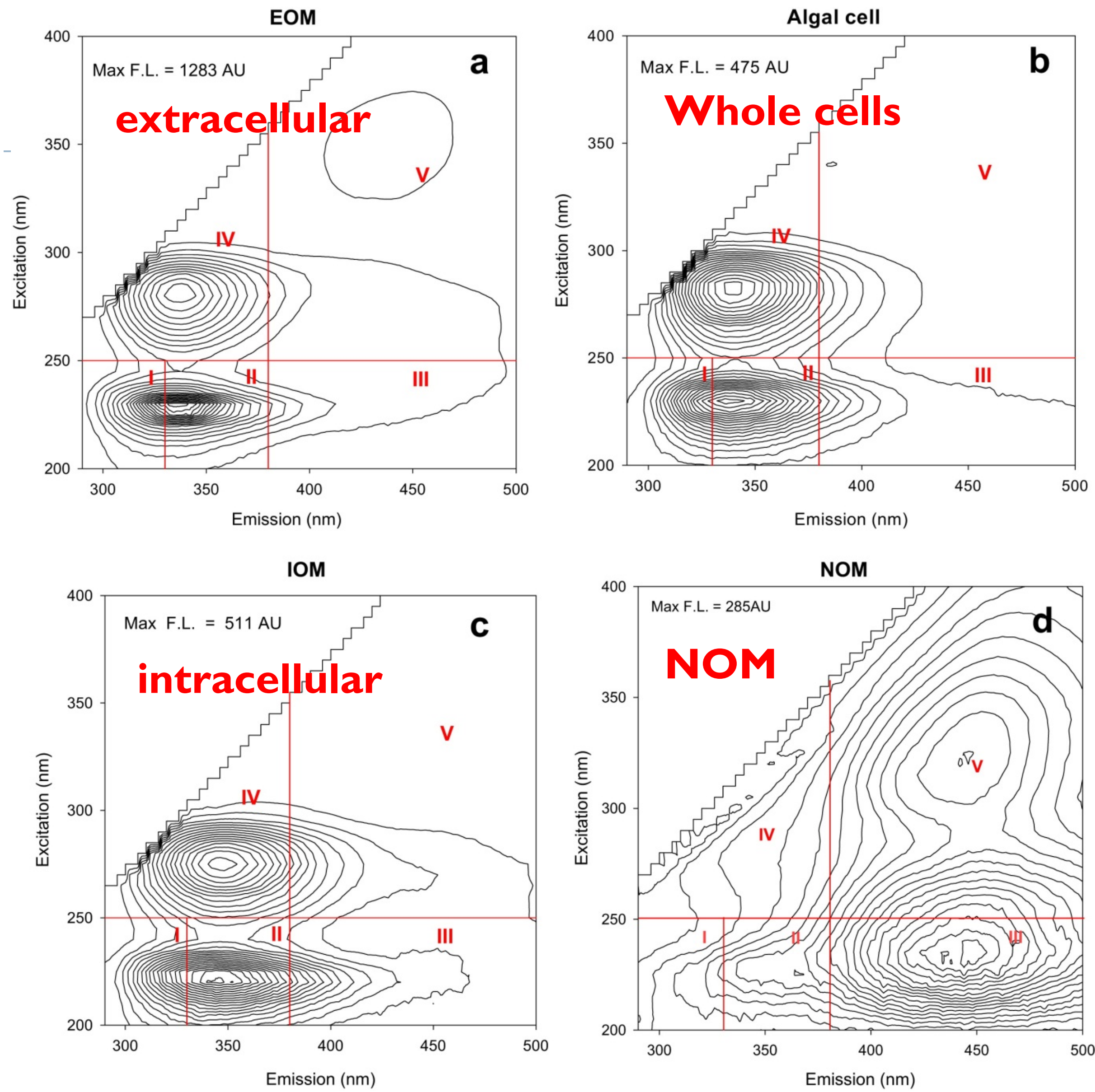
Correlation Between TTHMFP and UV absorbance for an Aquatic Fulvic Acid Subject to Coagulation at Various Alum Doses and various pHs (5-9) (from Reckhow, 1984)



Algal Organics

Microsystis aeruginosa

I: protein-like
II: protein-like
III: humic-like
IV: protein-like
V: humic-like



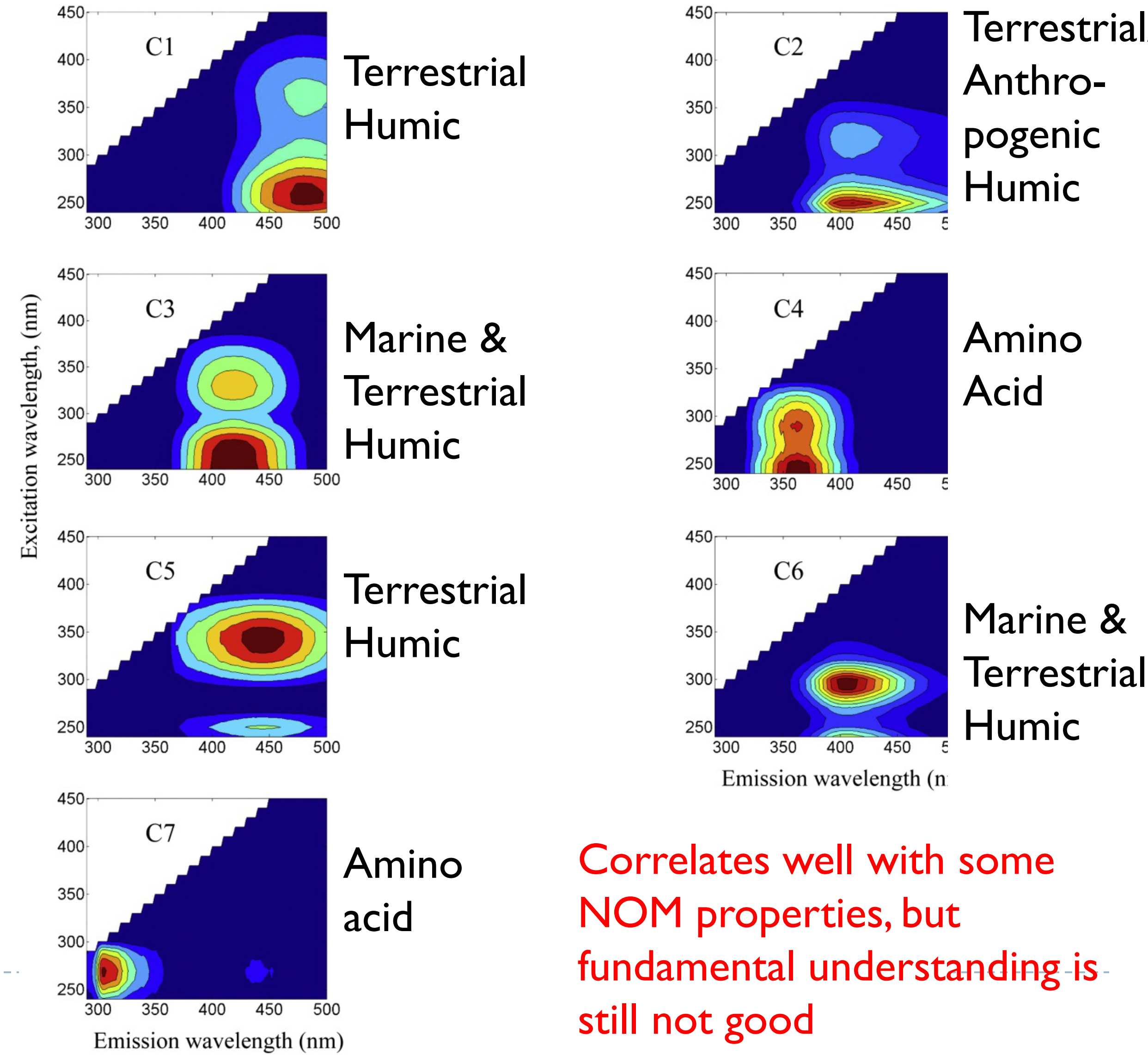
Fang et al., 2010

Fluorescence - EEMs

<u>Excitation-Emission Matrices</u>: Fluorescence intensity across the range of emission wavelengths while also scanning across excitation wavelengths

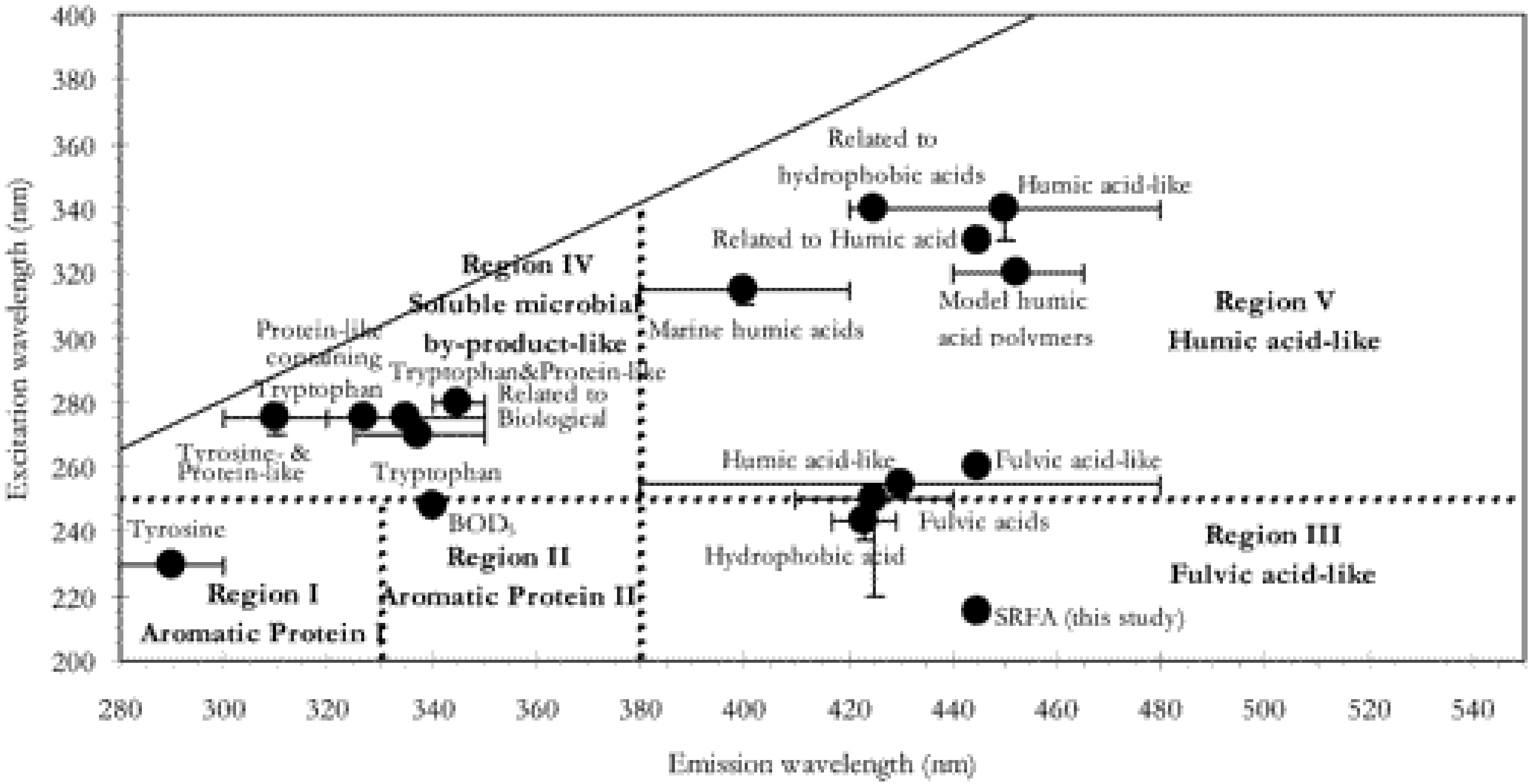
Contour plots of 7 components identified from the complete F-EEMs dataset.

Baghoth et al., 2011



Correlates well with some NOM properties, but fundamental understanding is still not good

Assignment of EEM Regions



Location of EEM peaks (symbols) based on literature reports and operationally defined excitation and emission wavelength boundaries (dashed lines) for five EEM regions

Chen et al., 2003

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

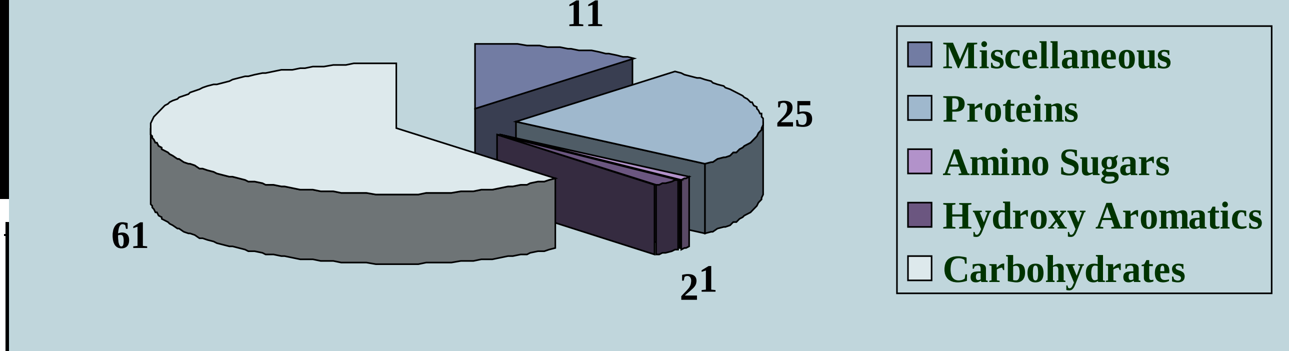
  .proteins (form pyrroles, indoles, phenol, p-cresol, nitriles)

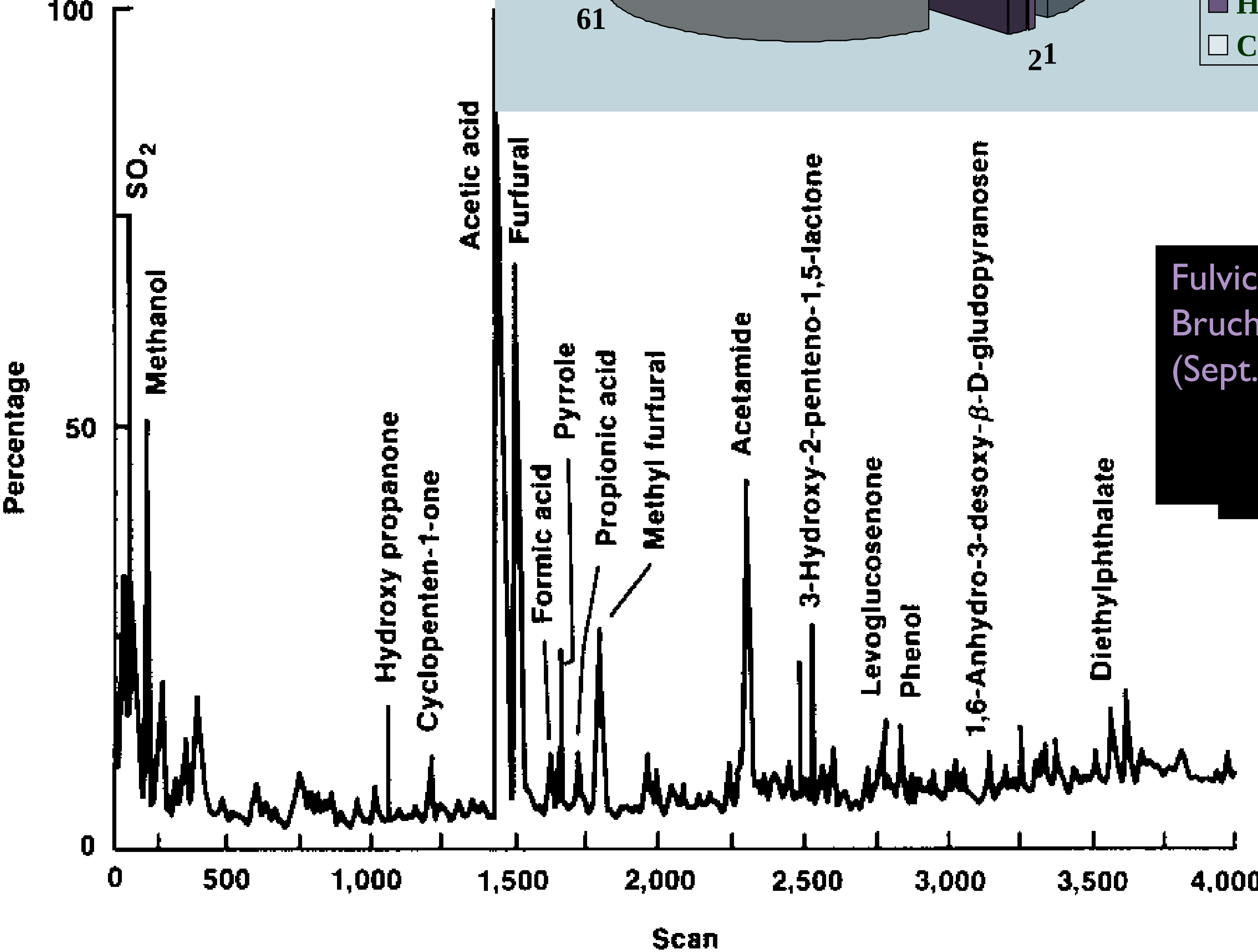
  .amino sugars (form acetamide)

  .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

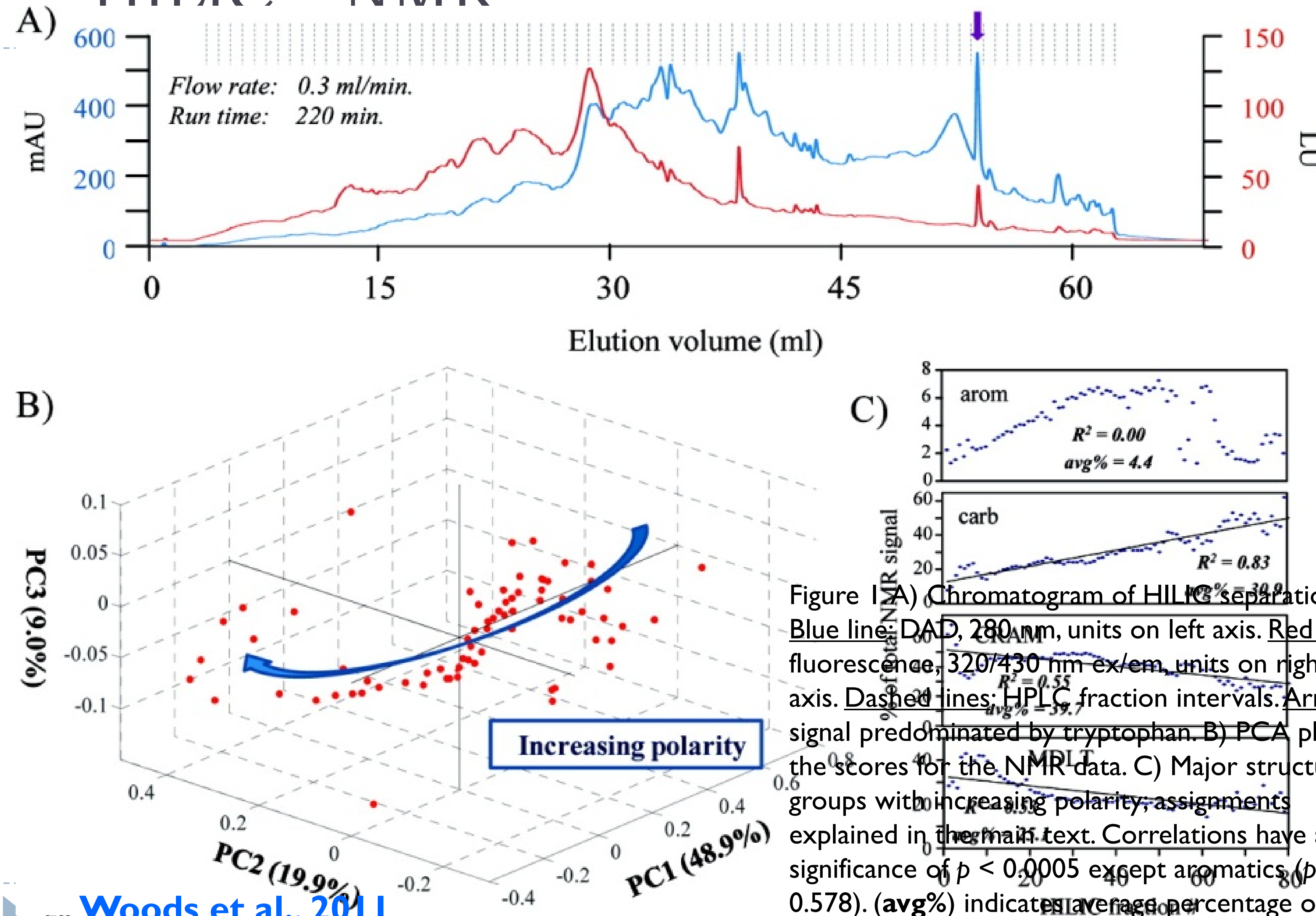
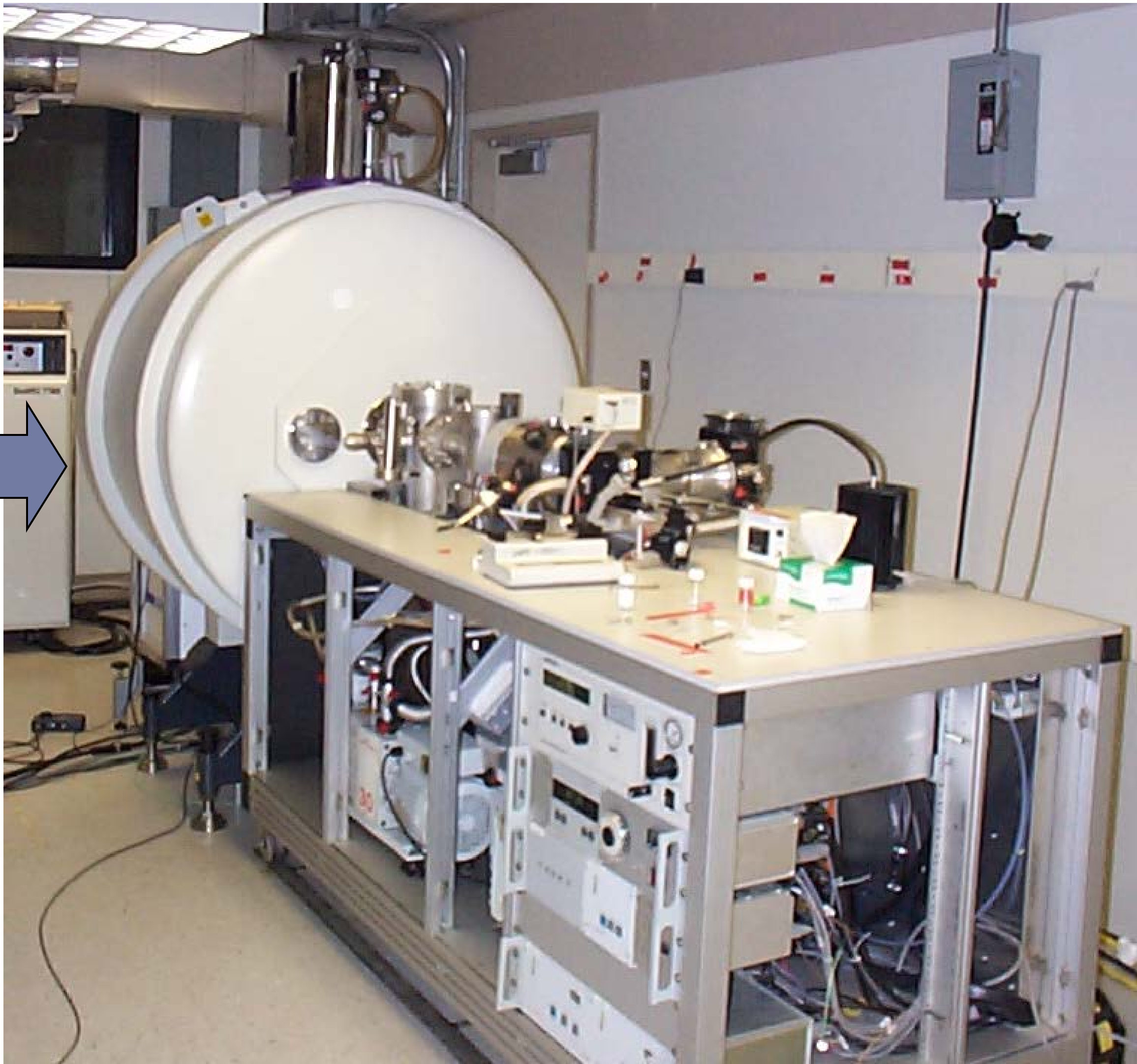


Figure 1 A) Chromatogram of HILIC separation. Blue line: DAD, 280 nm, units on left axis. Red line: fluorescence, 320/430 nm ex/em, units on right axis. Dashed lines: HPLC fraction intervals. Arrow: signal predominated by tryptophan. B) PCA plot of the scores for the NMR data. C) Major structural groups 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

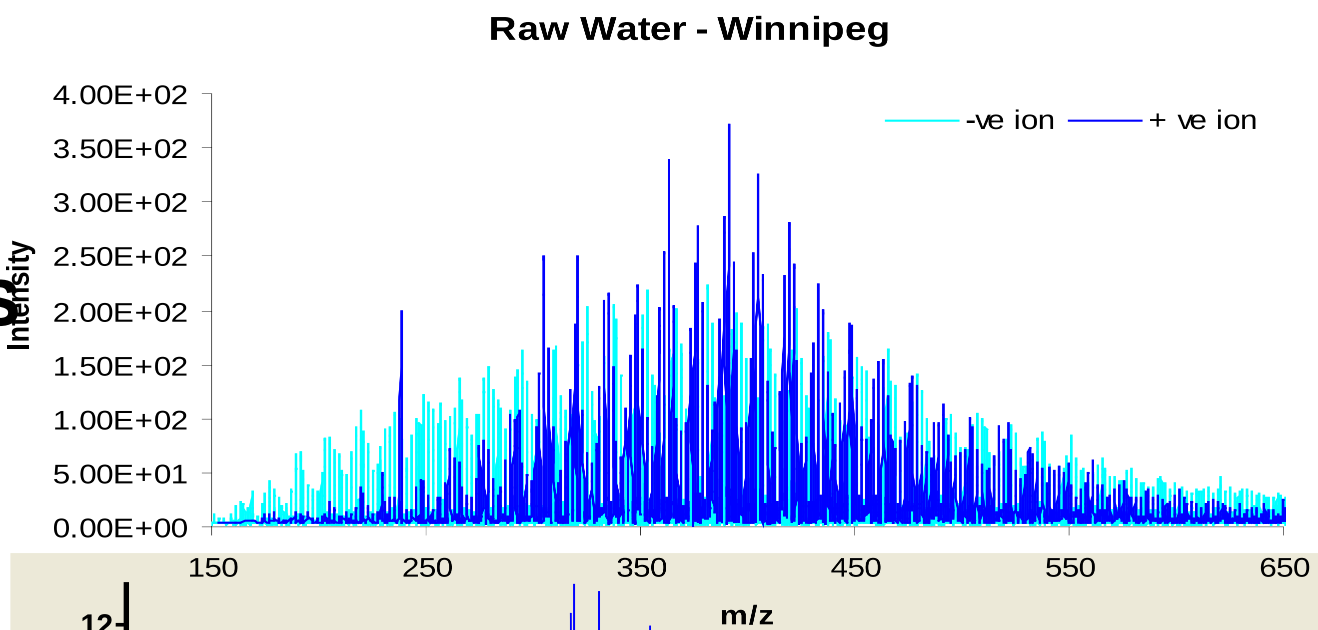
Woods et al., 2011

The Future??: Higher MW ID

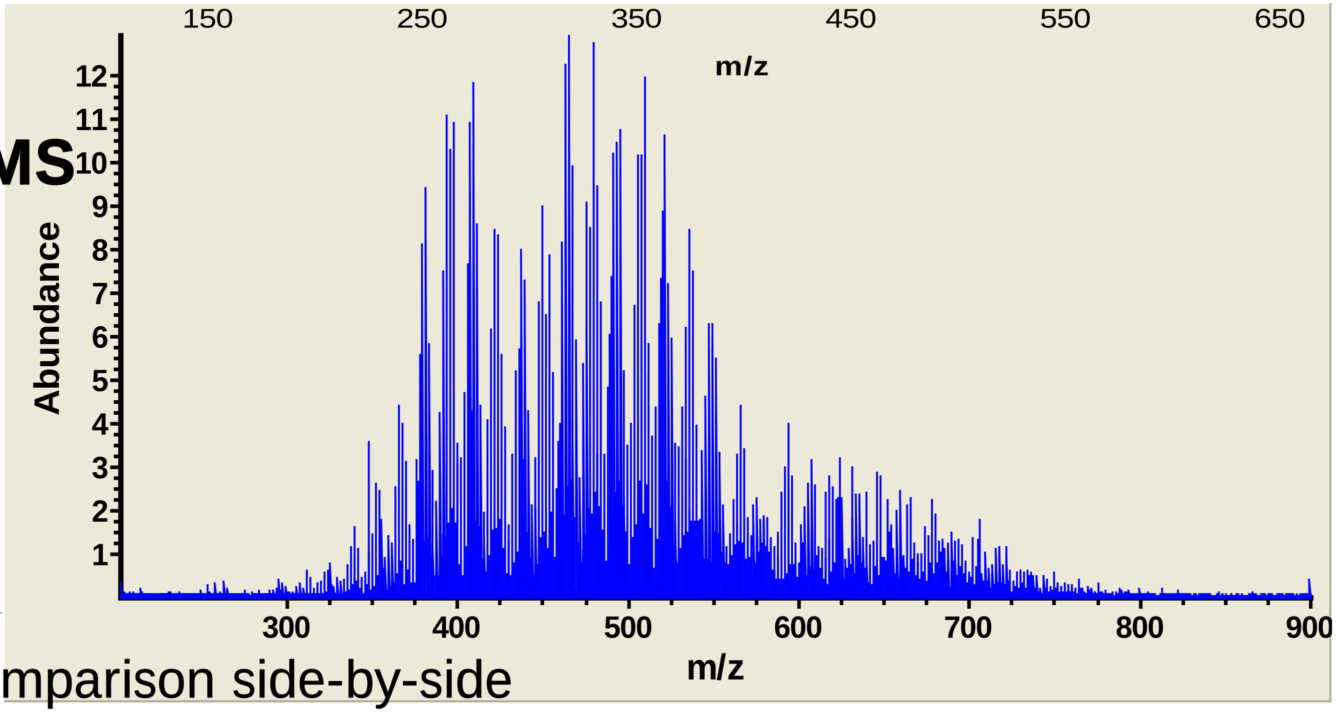
- NOM research
  - ESI with Ultra High-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Benefits
  - Unambiguous molecular formulae



ESI-TOF MS

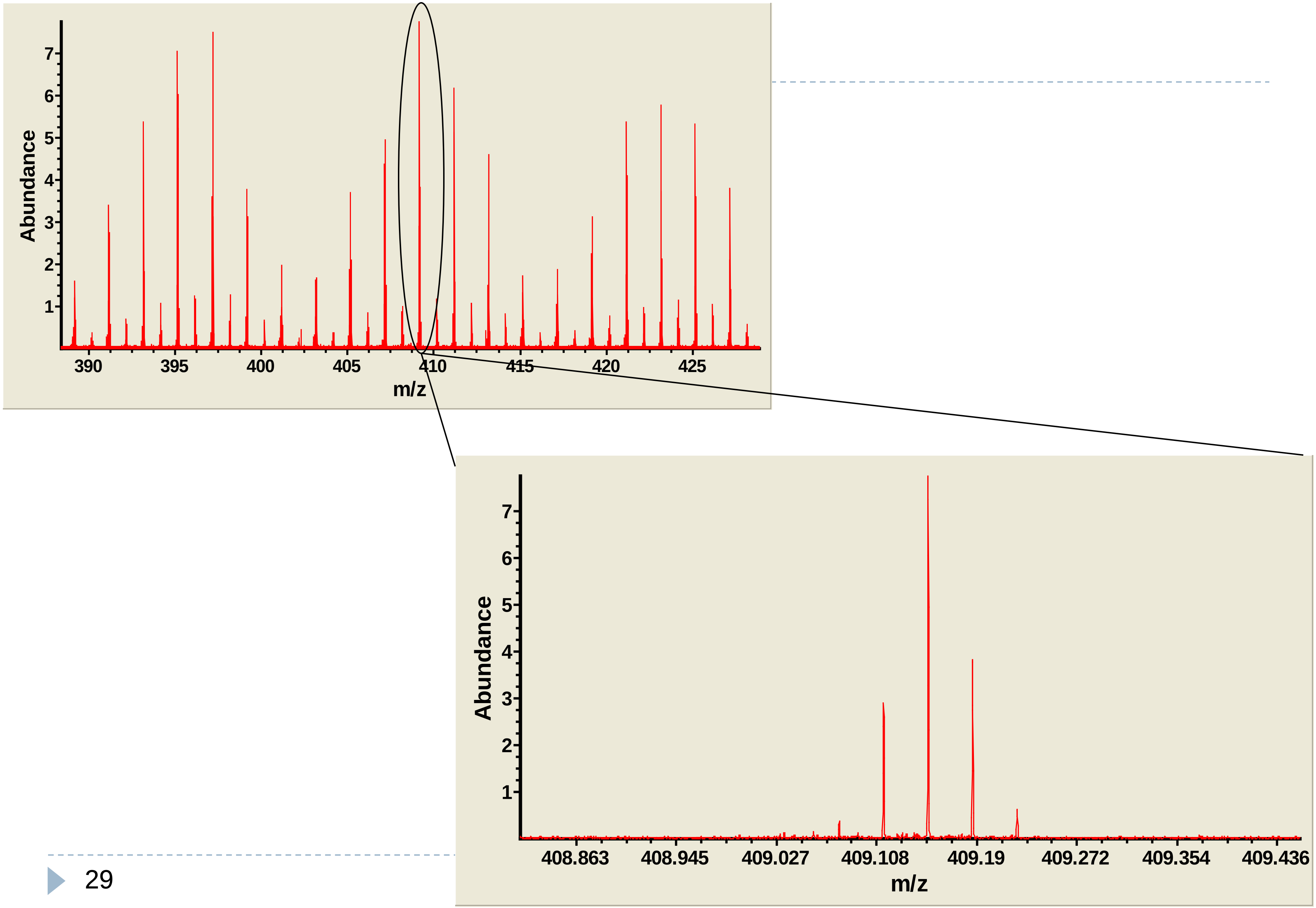


ESI-FTICR MS



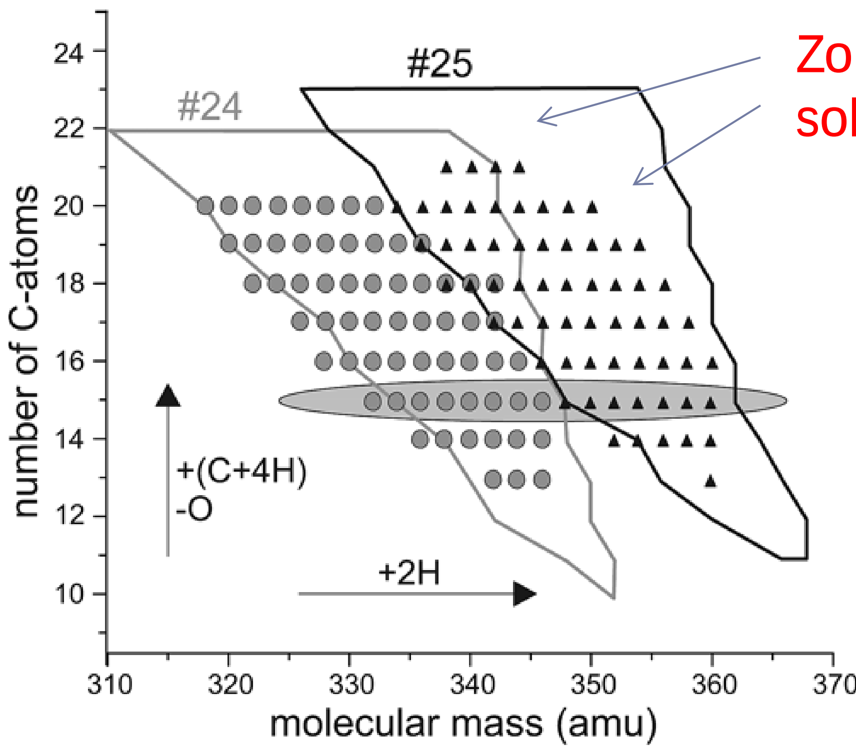
Same: comparison side-by-side

Chlorinated Water + Br Winnipeg

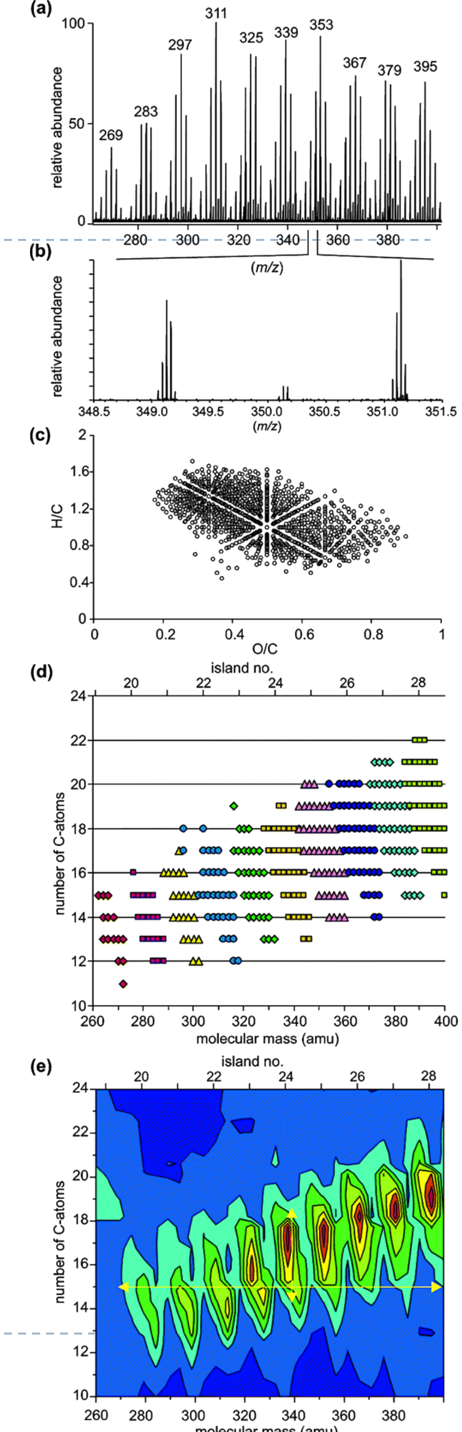


Ultra-high resolution MS

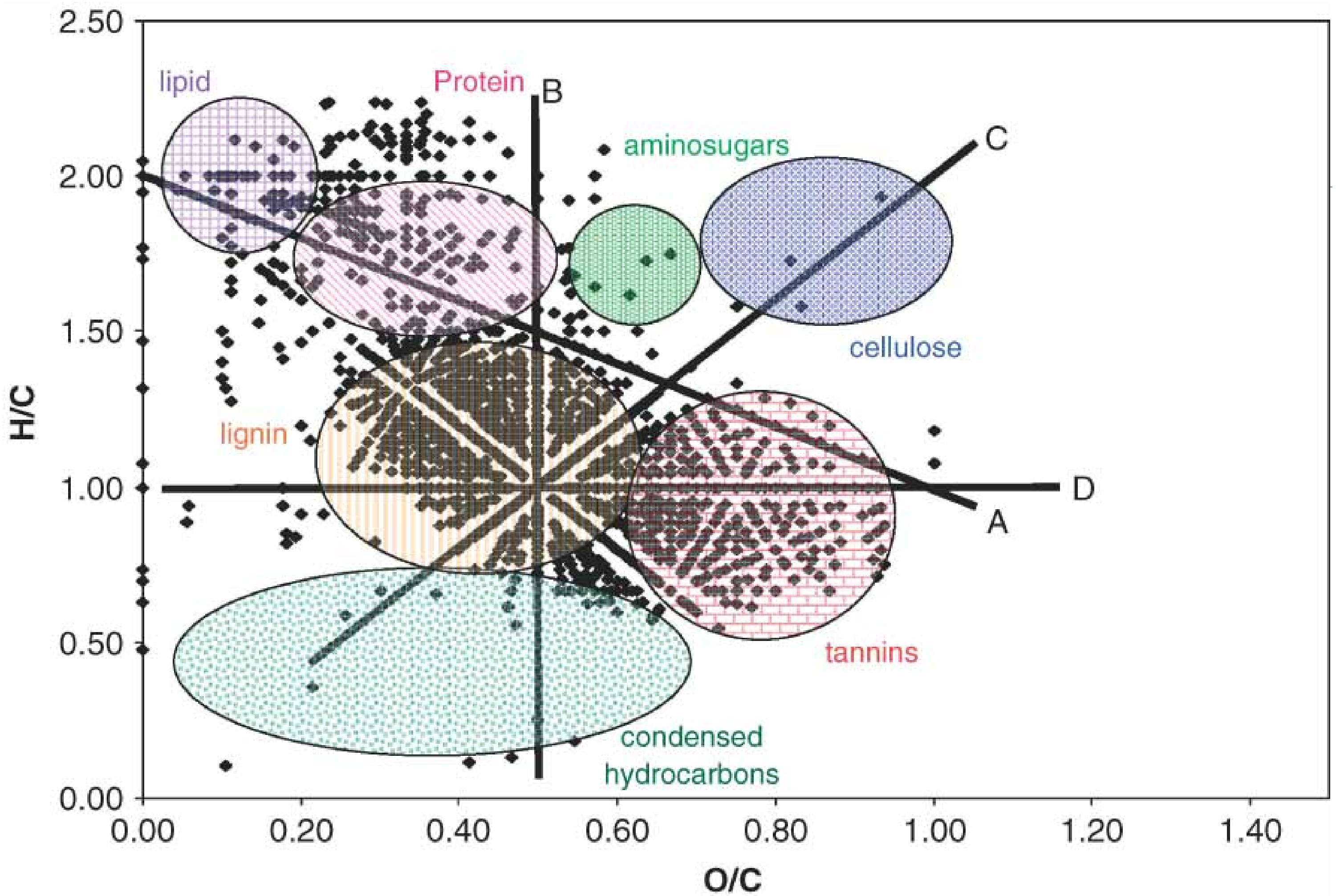
Reemtsma et al., 2006 [ES&T: 40:19:5839]



Zone of low solubility



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)).

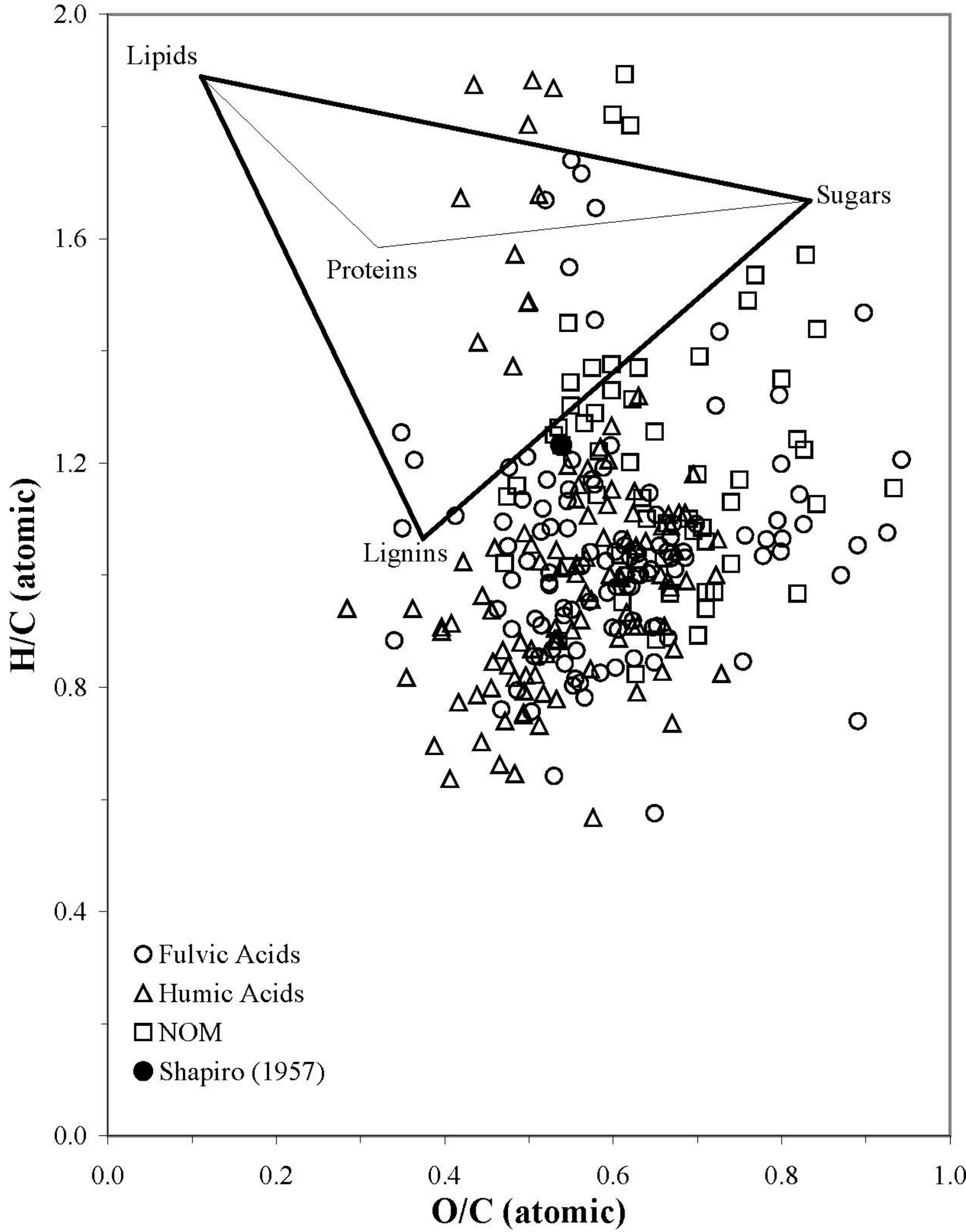


- Van Krevelen diagram for the Dismal Swamp DOM, compound classes are represented by the circles overlain on the plot. The distinctive lines in the plot denote the following chemical reactions: (A) methylation/demethylation, or alkyl chain elongation; (B) hydrogenation/dehydrogenation; (C) hydration/condensation;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

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

Elemental Ratios

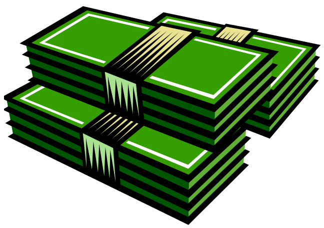
- Van Krevelen Plot



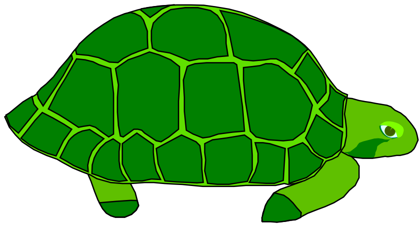
From:
Perdue & Ritchie, 2004

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