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CEE 697z
Organic Compounds in Water and Wastewater

NOM Characterization I

Lecture #7

Outline

- Many ways to "slice the NOM Pie"
- Concentrations
- Characteristics
  - Size, elemental composition, functional groups
- Structures
  - Mass spectrometry with and without various levels of degradation
- General Reactivity

It's one of my favorite recipes. I call it Fulvic Acid

I. NOM Structure & Selected Properties

- A. Bulk Organic Matter
  - occurrence
  - simple bulk properties
    - Elemental analysis
    - absorbance
  - Know structural elements
    - bulk functionality
    - specific structures
  - General reactivity with treatment chemicals
    - THM FP, other DBP FPs

Will discuss this later

II. NOM Structure (cont.)

- B. NOM from specific source types
  - 1. allochthonous or pedogenic
    - lignins & non-humics
  - 2. autochthonous or aquogenic
    - algal (AOM)
  - 3. wastewater effluent organics (EfOM)
    - soluble metabolic products
  - 4. Major biochemical constitutents
    - lignin, proteins, terpenoids, tannins, others

In many cases we have the same characterization s for these groups that we have for the bulk organic mater

III. NOM Structure (cont.)

- C. Subcomponents from bulk NOM
  - hydrophobic acids (humics)
    - humic and fulvic acids
  - Hydrophilic acids
    - meso to philic to ultra
  - Neutral fractions
    - phobic, philic
  - Base fractions
    - phobic, philic

In many cases we have the same characterization s for these groups that we have for the bulk organic mater

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

TOC analysis

Principle: oxidize all organic matter to Carbon dioxide and water. Then measure the amount of carbon dioxide produced

$$C_aH_bN_cO_d + (a + \frac{b}{4} - \frac{d}{2})O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2$$

Oxidation

- High Temperature Pyrolysis
- UV Irridiation
- Heated Persulfate
- UV/Persulfate

Particulate-C vs. Dissolved-C

- Particulate organic carbon
  - larger than about 1 micron
  - determined by what is retained in laboratory filtration
  - algae, bacteria, protozoa, organics adsorbed to clays
- Dissolved organic carbon (DOC)
  - from simple molecules to large biopolymers
  - determined from the TOC of a filtered sample
  - typically comprises 90-98% of the TOC

Fractionation & Nomenclature

Total Carbon (TC)

Inorganic Carbon (IC)

Total Organic Carbon (TOC)

Purgeable (Dissolved)

Non-Purgeable (Particulate)

Purgeable Organic Carbon (POC)

Non-purgeable Organic Carbon (NPOC)

Particulate

Dissolved

(PtOC)

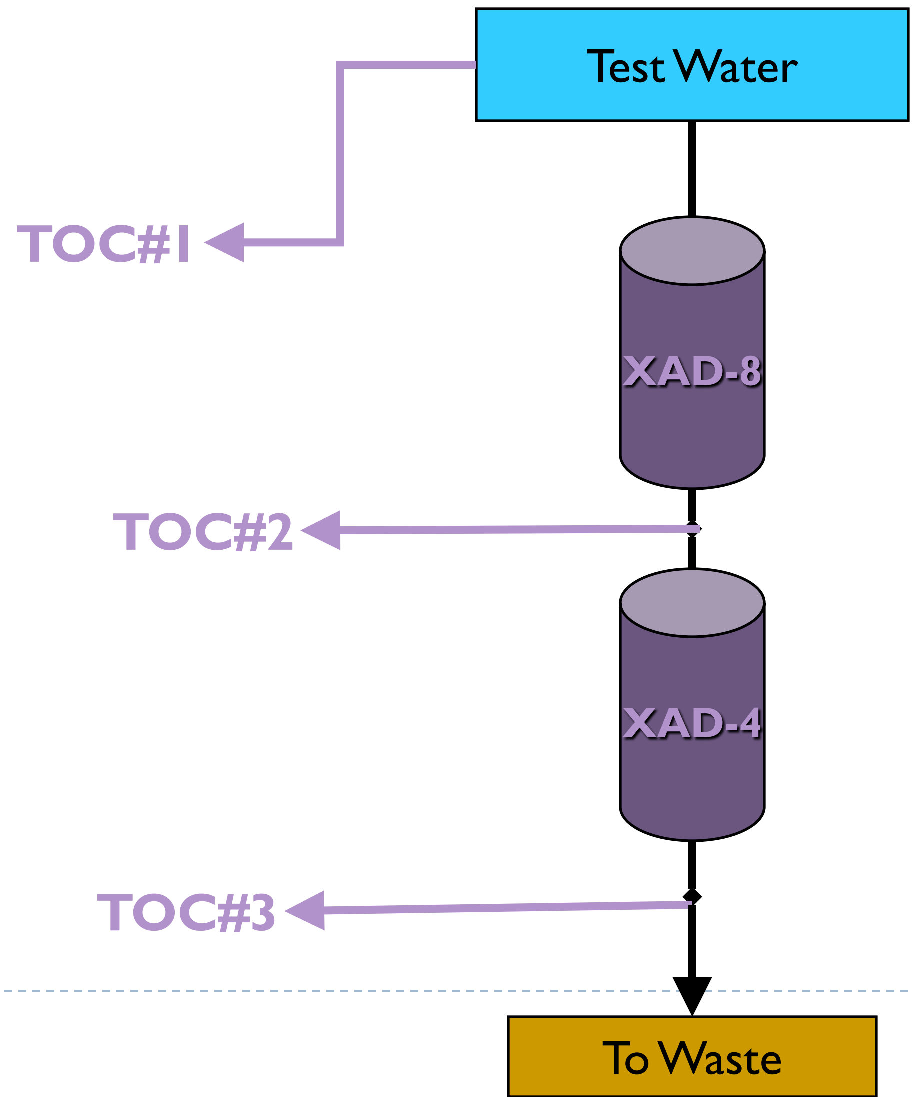
(DOC)

Methods of Fractionation

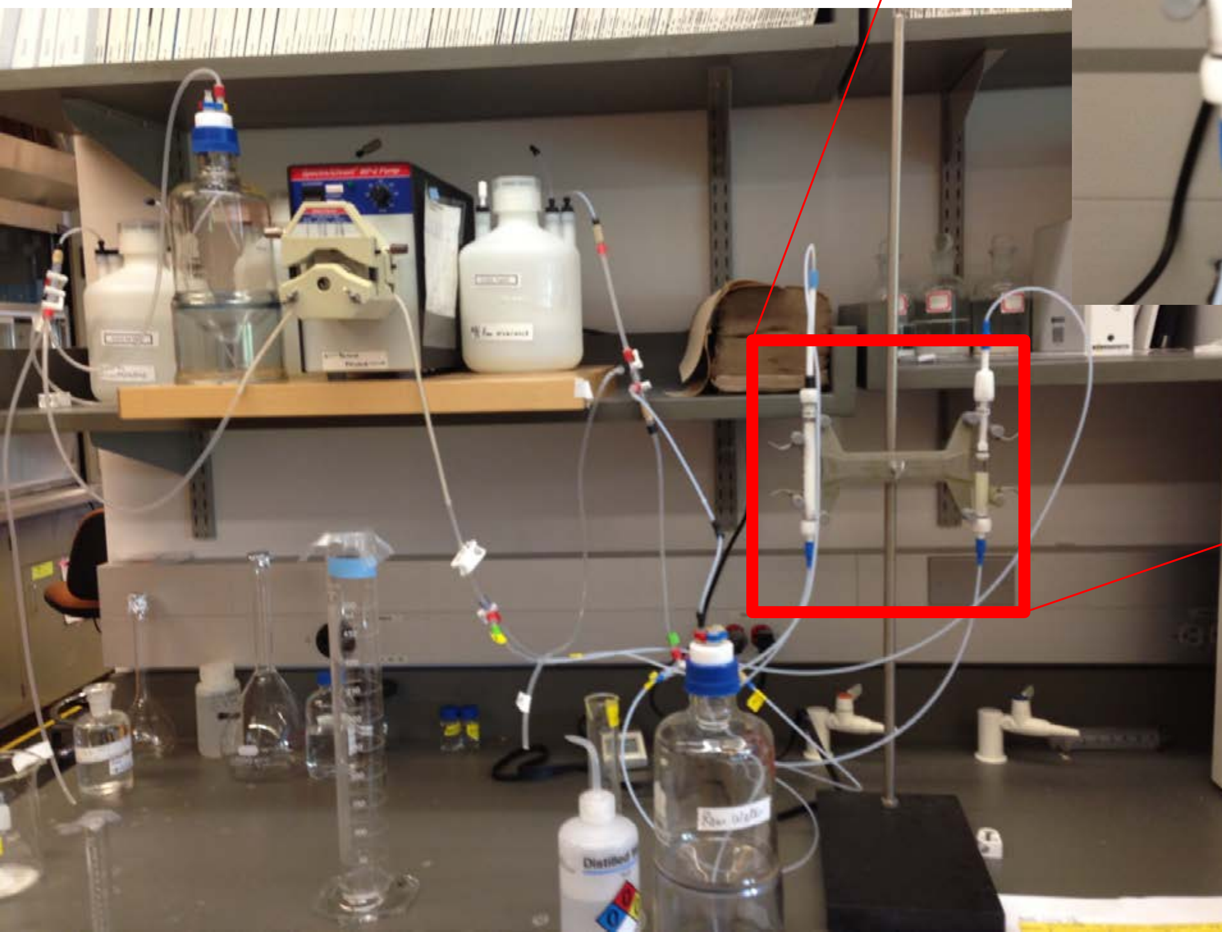
- Resin-based
  - Usually XAD resins
  - May combine with ion exchange resins
- Evaporative or RO
- RO & ED
  - Drewes et al., 2002 WQTC
  - Perdue

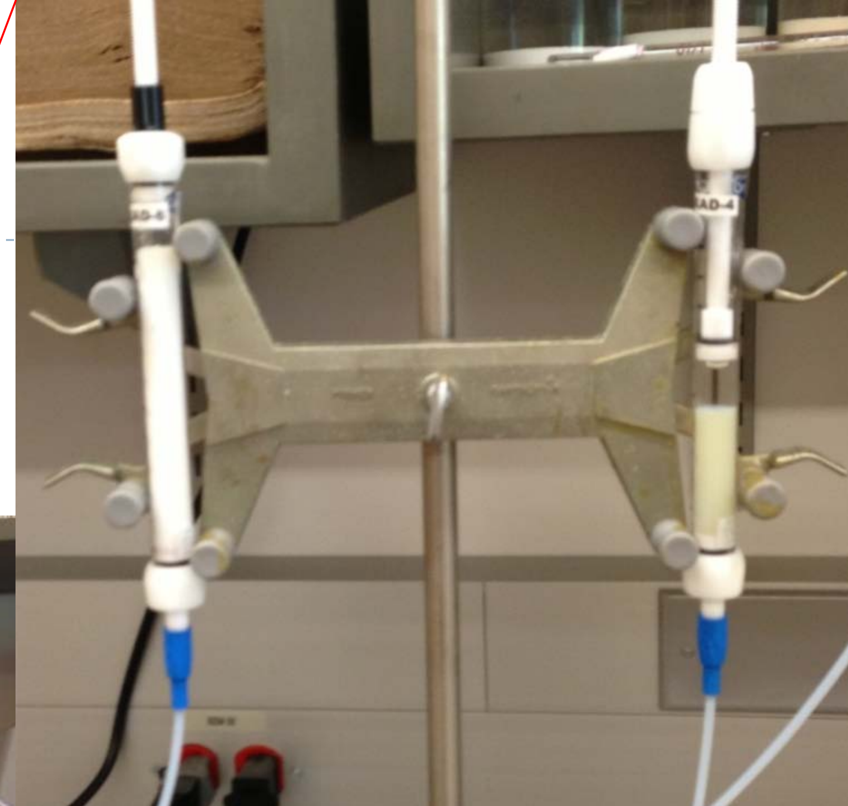
Simple Hydrophobicity Test

- Hydrophobic NOM
  - Retained on XAD-8
    - TOC#1-TOC#2
- Mesophilic NOM
  - Retained on XAD-4, but not on XAD-8
    - TOC#2-TOC#3
- Hydrophilic NOM
  - Not retained
    - TOC#3



Mini-XAD Lab setup





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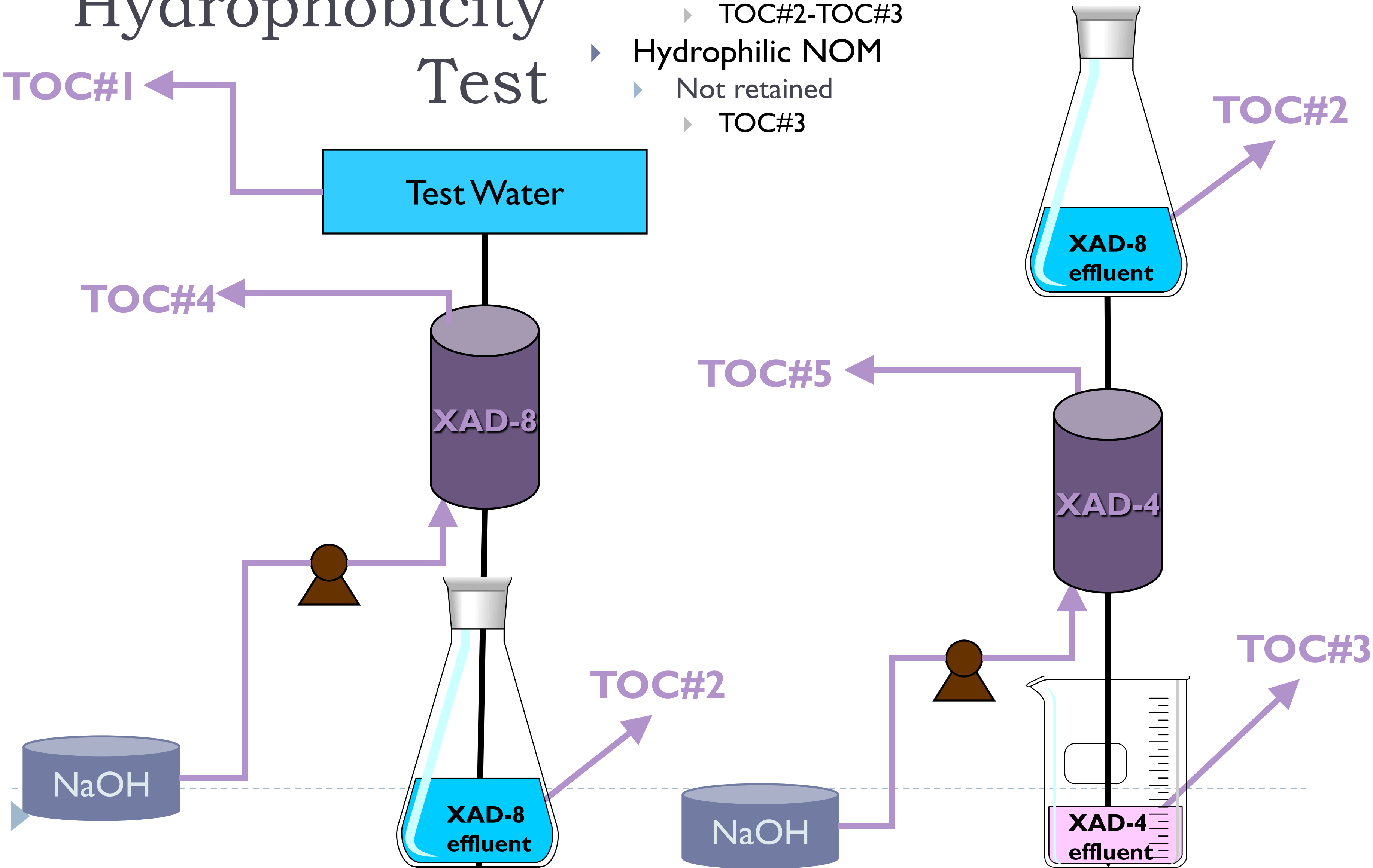
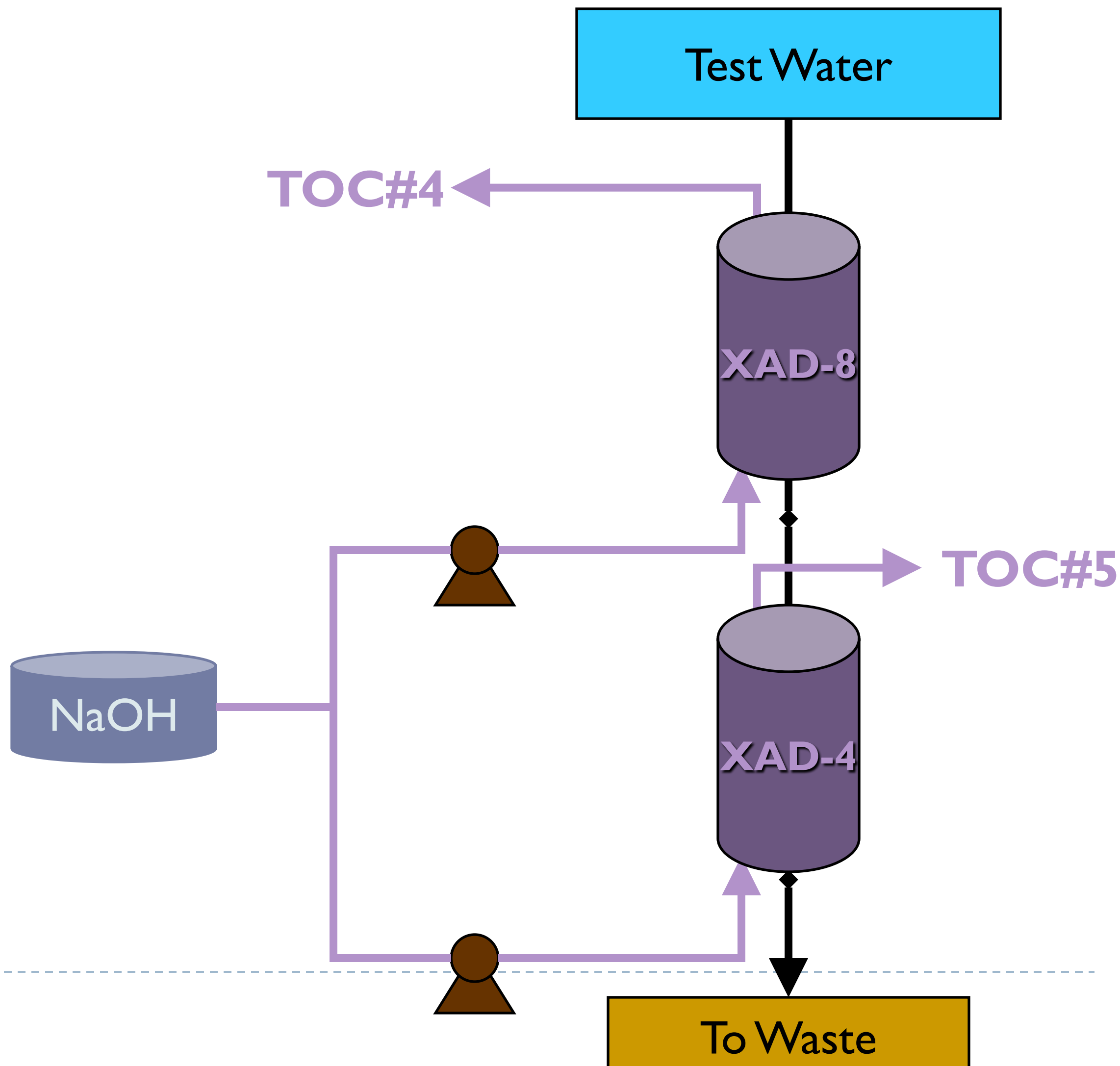
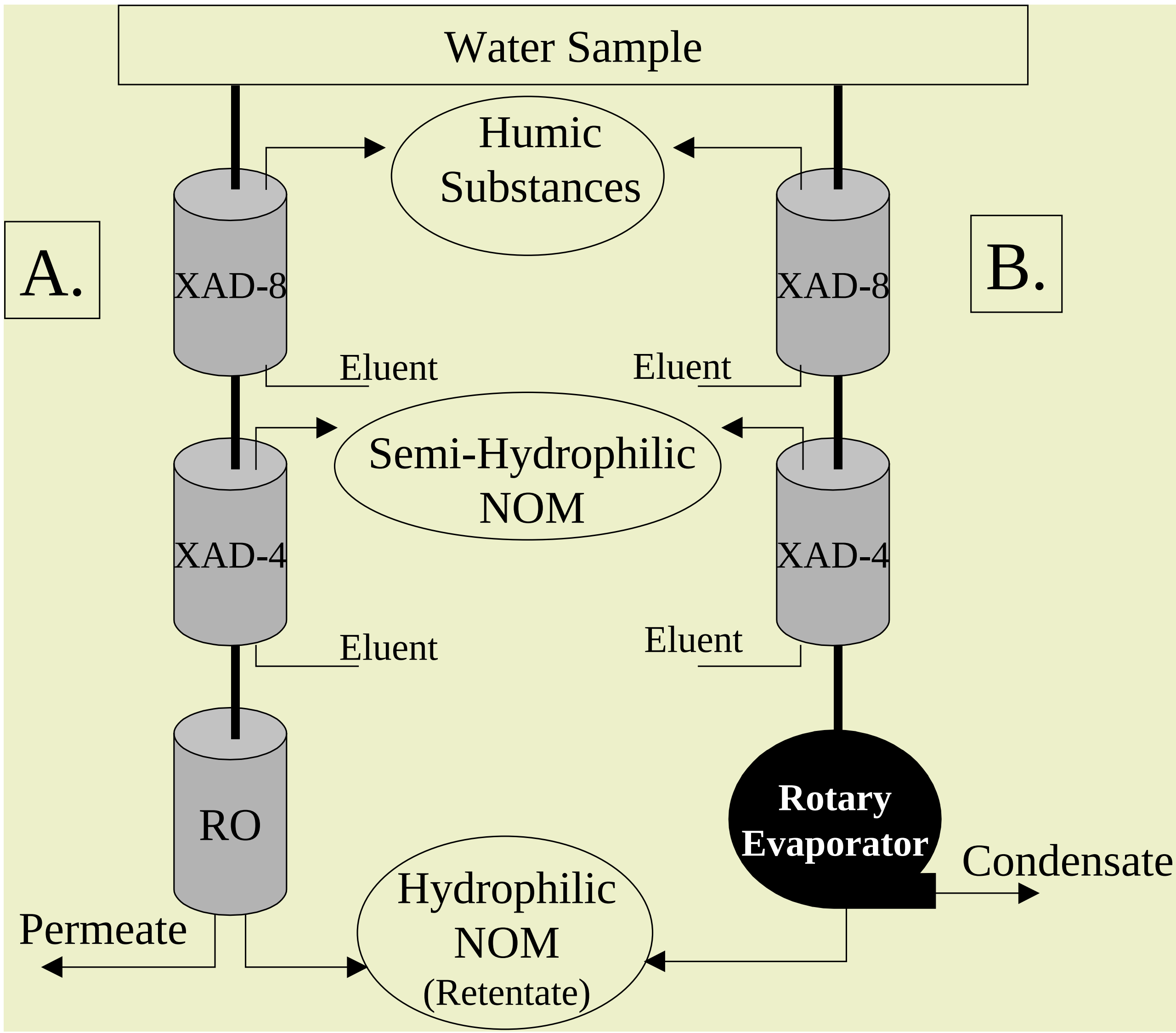


Simple Hydrophobicity Test #2

- Back elution with NaOH
- Allows recovery of fractions and check of direct fractionation
- Desorbable hydrophobics = TOC#4
- Desorbable mesophilics = DOC #5

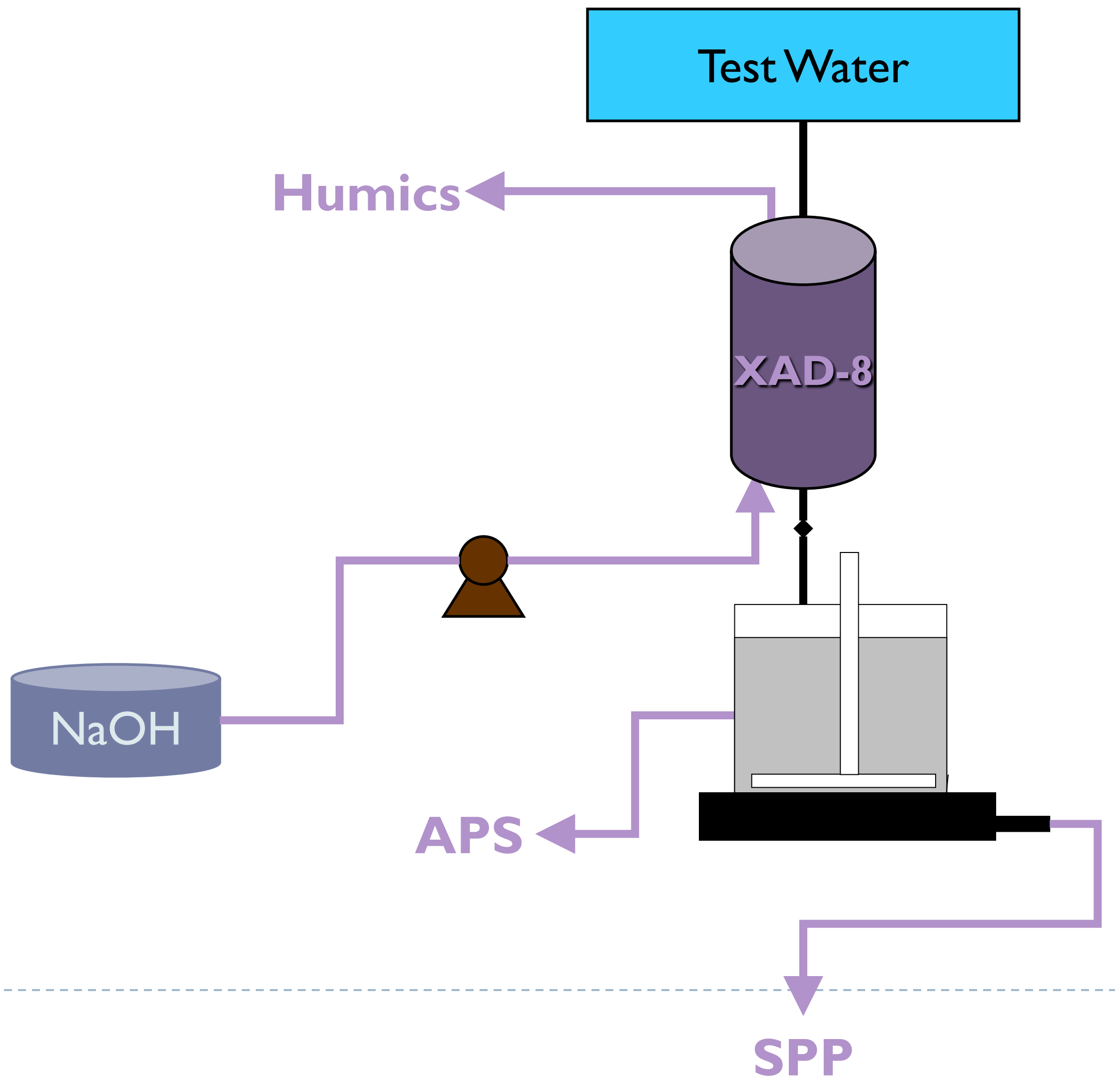


Analysis of Hydrophobicity



NOM Pool Fractionation

- Back elution with NaOH
- Allows recovery of fractions and check of direct fractionation
- Humics elute from XAD-8
- APS from UF
- SPP is not retained



Polarity Rapid Assessment Method (PRAM)

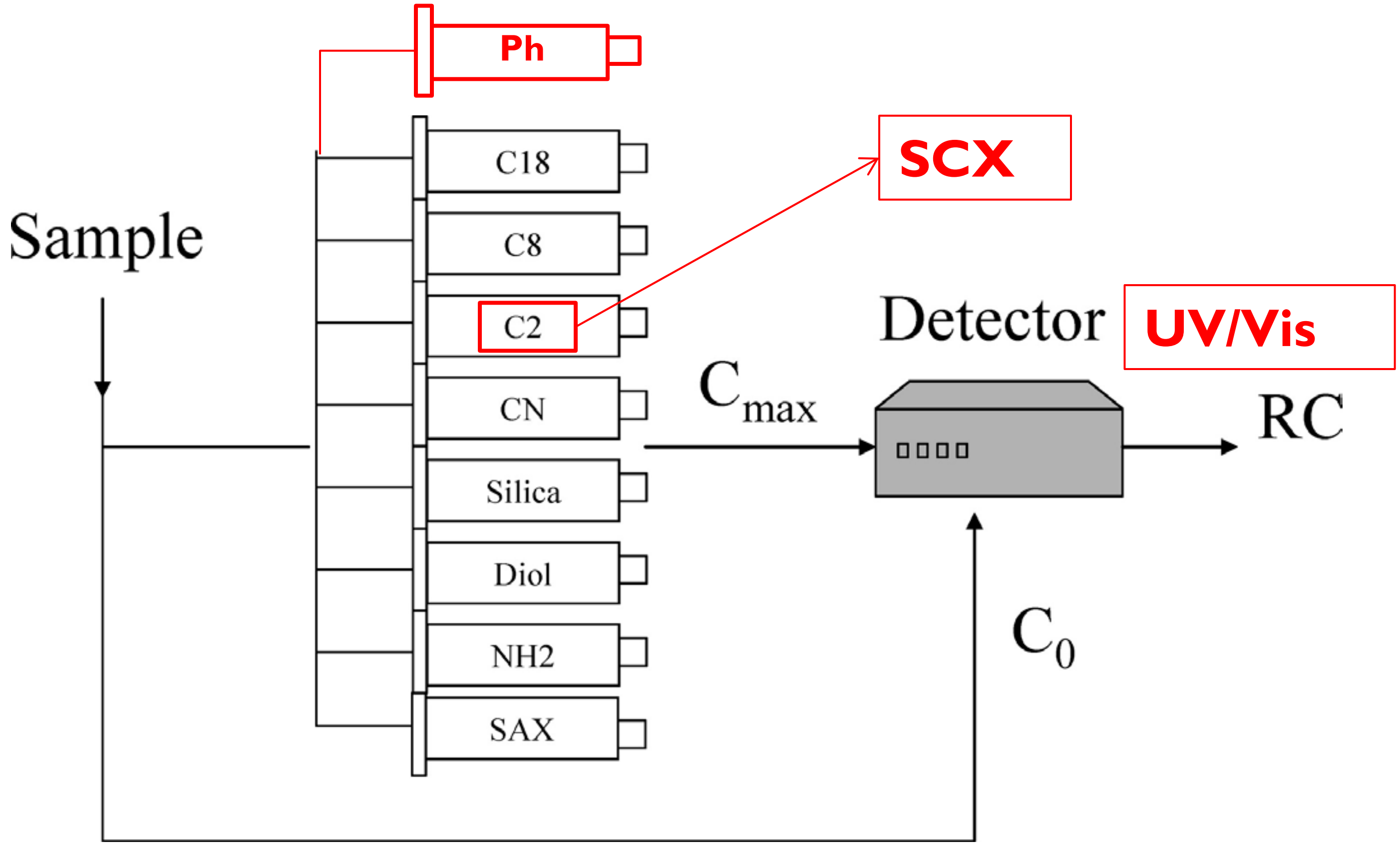
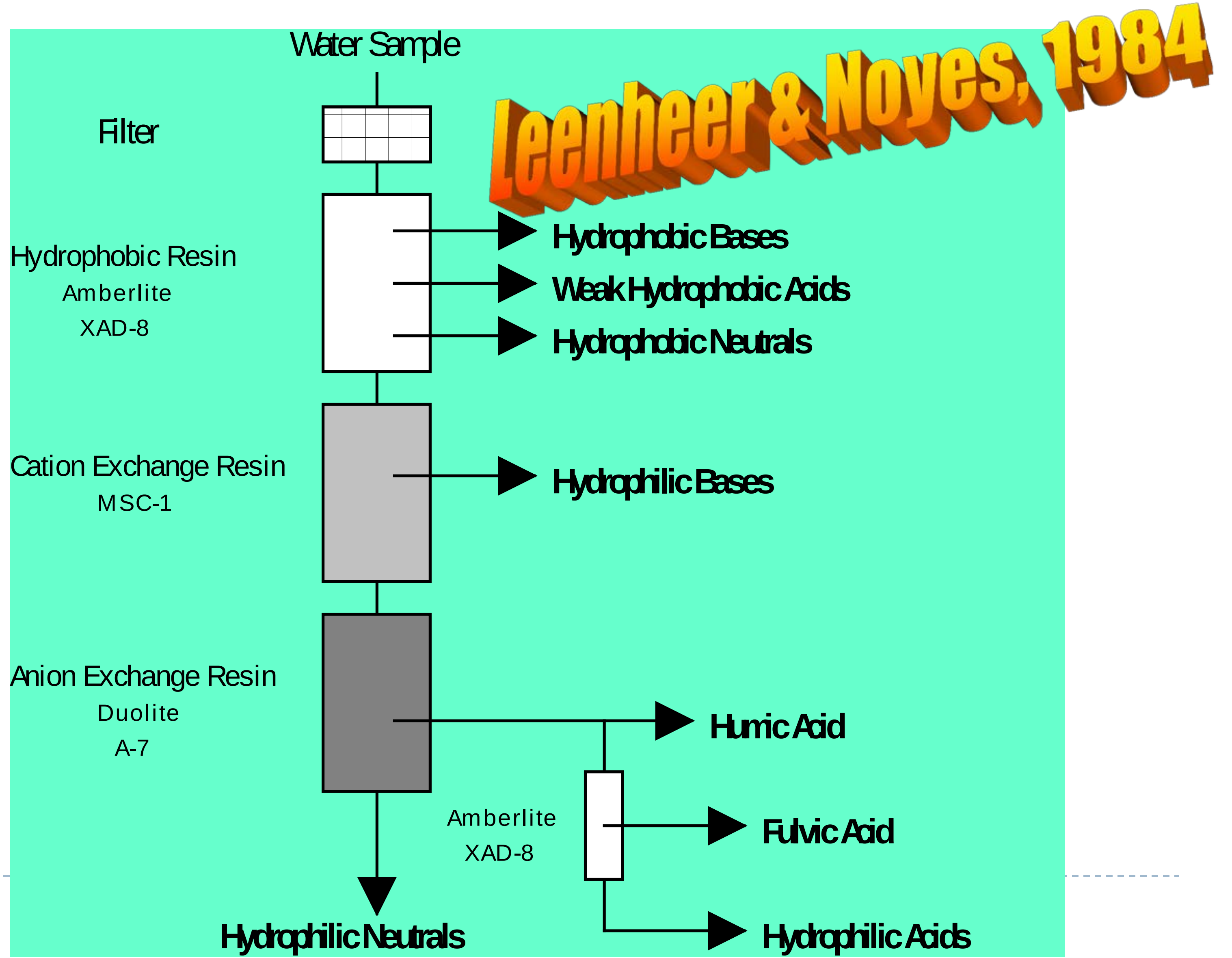


Figure 1 Experimental setup for PRAM. SPE cartridges contained 100 mg of sorbent with a total volume of 1.5 mL and average pore size of 60 Å. The retention coefficient (RC) is calculated based on the maximum breakthrough concentration and the initial concentration. C-18, C-8, and C-2 are nonpolar sorbents; Silica, Diol, and Cyanide (CN) are polar sorbents; Amino (NH-2) is a weak anion exchange and SAX is the strong anion exchanger.

Differences between UMass method and the Rosario-Ortiz method are in red

Published in: Fernando L. Rosario-Ortiz; Shane Snyder; I. H. (Mel) Suffet; *Environ. Sci. Technol.* **2007,** 41, 4895-4900.
DOI: 10.1021/es062151t

The Humics and Non-humics: Comprehensive NOM Fractionation



Proposed Assignments for Organic Fractions

Fraction	Composition
Colloidal	Bacterial peptidoglycan cell wall components (hydrophilic neutral)[1]
Hydrophobic	
Acids	
Weak	tannins; phenols; intermediate MW alkyl monocarboxylic acids (C5-C8), dicarboxylic acids (C8-C11)
Strong	fulvic acids; humic acids; high MW alkyl monocarboxylic acids (≥C9), and dicarboxylic acids (≥C12); aromatic acids
Bases	amphoteric proteinaceous materials; high MW (JC12) alkyl amines; alkyl pyridines; aromatic amines
Neutrals	hydrocarbons; high MW (≥C6) methyl ketones; furans; most ethers; high MW (≥C5) alkyl alcohols, and aldehydes; lactones; pyrrole, alkyl aromatic sulfonates[1]
Hydrophilic	
Acids	hydroxy acids; sugar acids; sulfonic acids; low MW alkyl monocarboxylic acids (C1-C4), and dicarboxylic acids (C2-C7)
Bases	low MW (C1-C11) alkyl amines; amino acids; purines; pyrimidines; pyridine; hydroxy pyridines
Neutrals	polysaccharides; Low MW (C1-C4) alkyl alcohols, aldehydes, and ketones; poly-ketones; amides, N-acetyl amino sugars[1], non-carbohydrate alcohols[1]

- +Based on: Leenheer and Noyes, 1984; Leenheer et al., 1982; and Reckhow et al., 1992

The Humic Substances

- Analytically defined
  - Humic & fulvic acids
- True structure is unknown — Many ideas
- Chemical Characterization
  - Elemental Composition
  - Aromaticity — High
  - Functional Groups — Moderate acidity
  - Molecular Size — Moderate
  - Absorbance — High

Elemental Composition: Humics

Elemental Composition of Aquatic Humic Substances

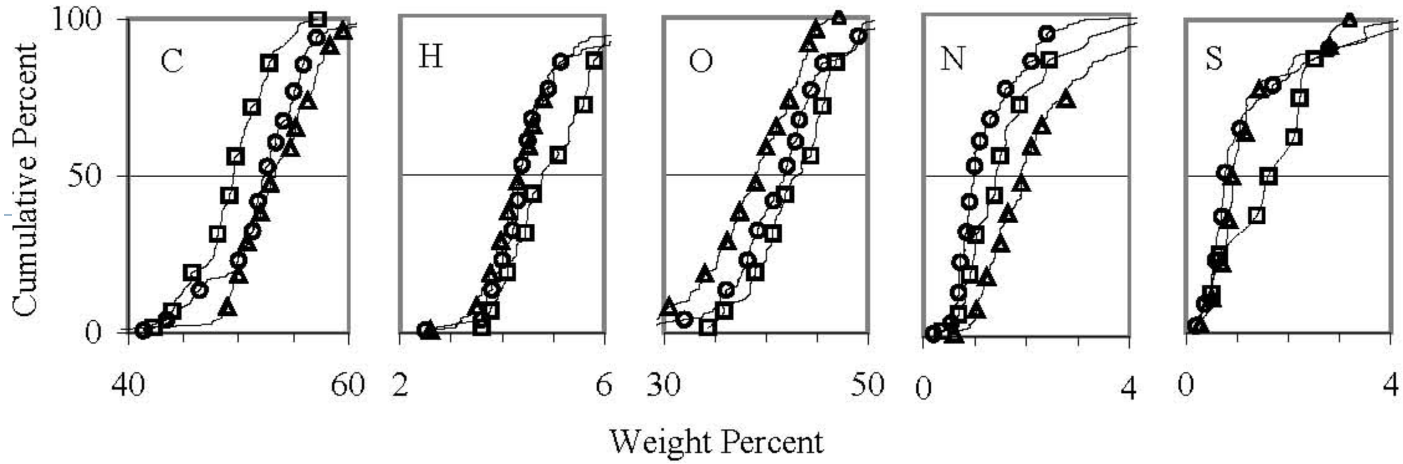
(average of 15 riverine samples, after Thurman, 1985)

Fraction	C	H	O	N	P	S	Ash
Fulvic	51.9	5.0	40.3	1.1	0.2	0.6	1.5
Humic	50.0	4.7	39.6	2.0			5.0

High oxygen content
FA and HA Similar, except:

- humics tend to have more N

Elemental Analysis

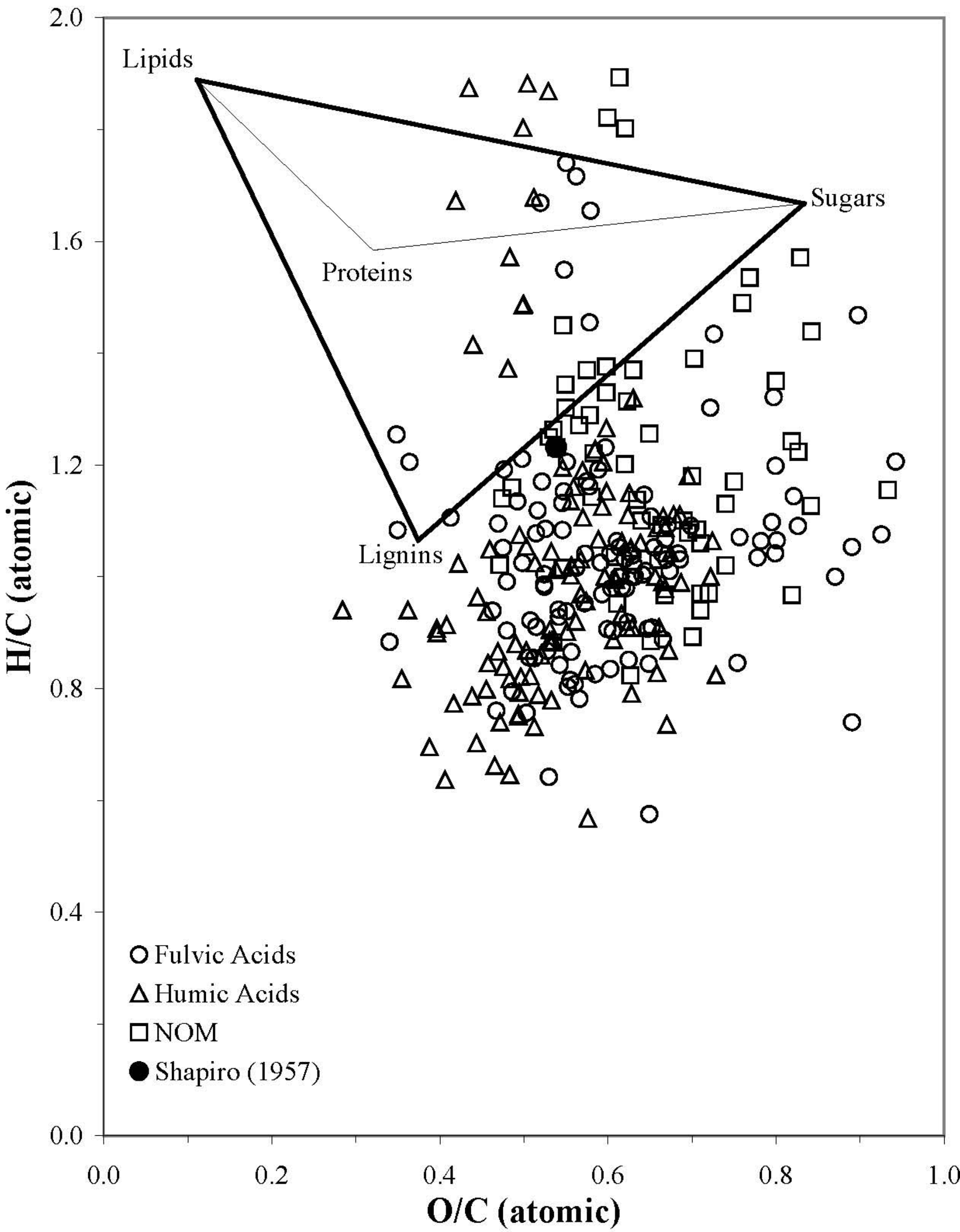


Element	Sample	Obs.	Weight Percent[a] Range	Median	Mean	Std. Dev.
	FA	117	41.4 - 62.7	52.3	52.1	4.2
Carbon	HA	107	38.7 - 62.7	53.3	53.4	3.9
	NOM	57	42.3 - 57.2	49.6	49.5	3.3
	FA	117	2.5 - 8.1	4.4	4.6	1.0
Hydrogen	HA	107	2.6 - 8.2	4.3	4.5	1.0
	NOM	57	3.6 - 7.9	4.8	5.0	1.0
	FA	117	27.5 - 52.1	41.9	41.5	4.9
Oxygen[b]	HA	107	23.5 - 47.2	39.1	38.5	4.9
	NOM	57	34.3 - 52.6	43.5	43.0	4.1
	FA	117	0.2 - 9.2	1.0	1.3	1.0
Nitrogen	HA	107	0.6 - 9.8	1.9	2.4	1.7
	NOM	57	0.4 - 5.4	1.4	1.7	1.0
	FA	43	0.2 - 4.3	0.8	1.2	1.0
Sulfur	HA	36	0.3 - 3.2	0.9	1.2	0.8
	NOM	8	0.5 - 4.7	1.9	2.0	1.3

From:
Perdue & Ritchie, 2004

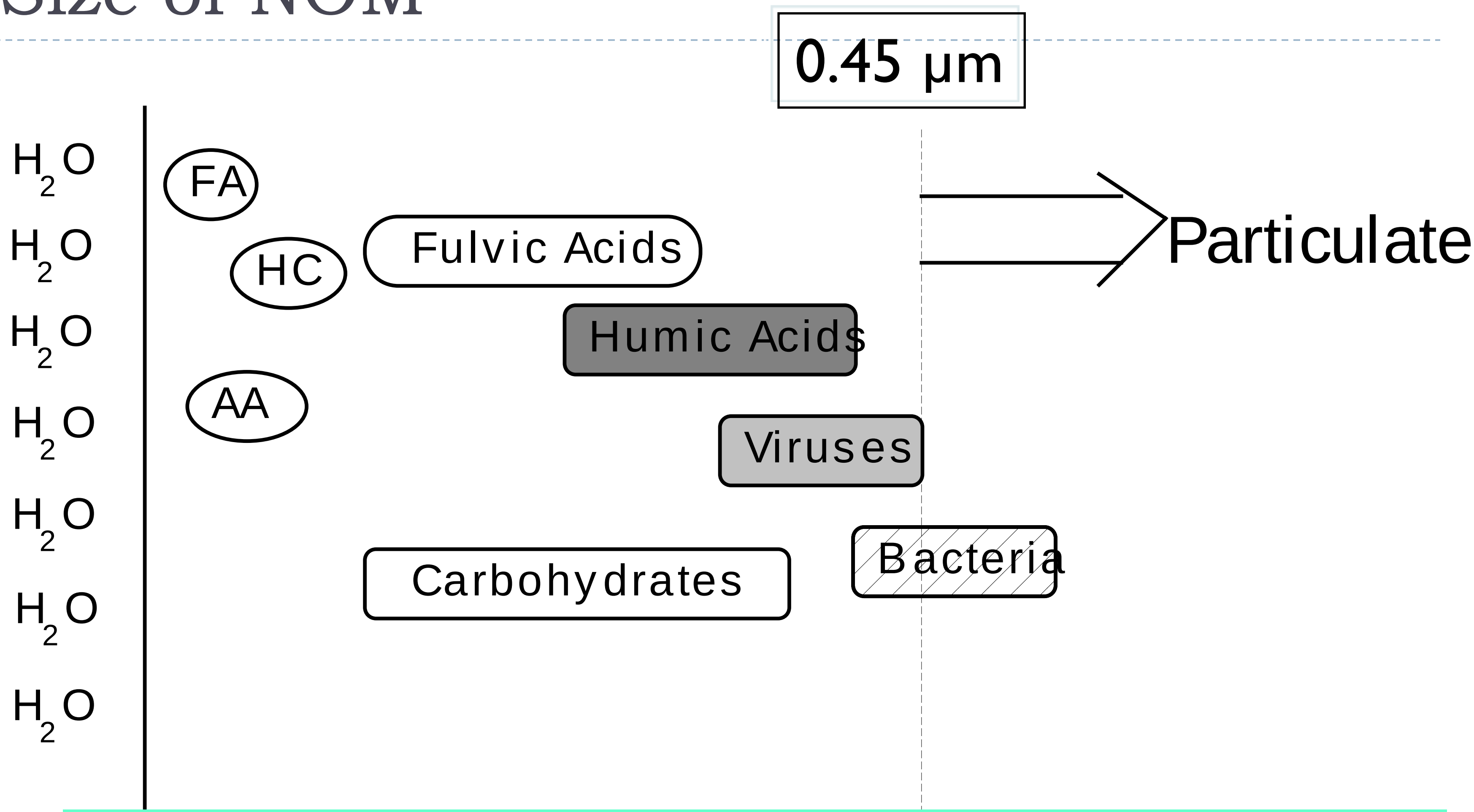
Elemental Ratios

- Van Krevelen Plot



From:
Perdue & Ritchie, 2004

Size of NOM

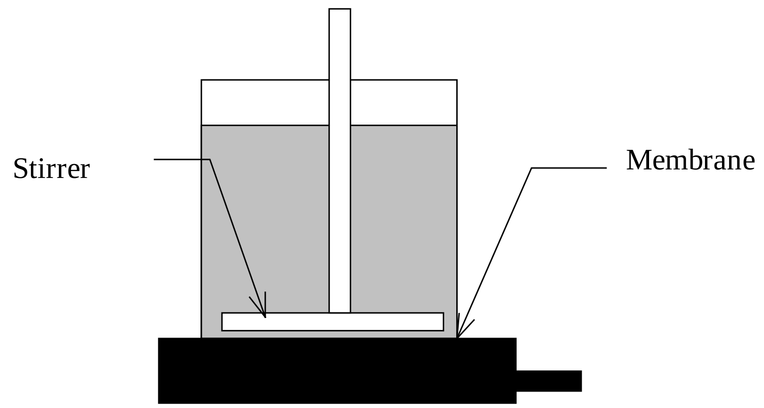


Relative Size of Natural Organic Carbon

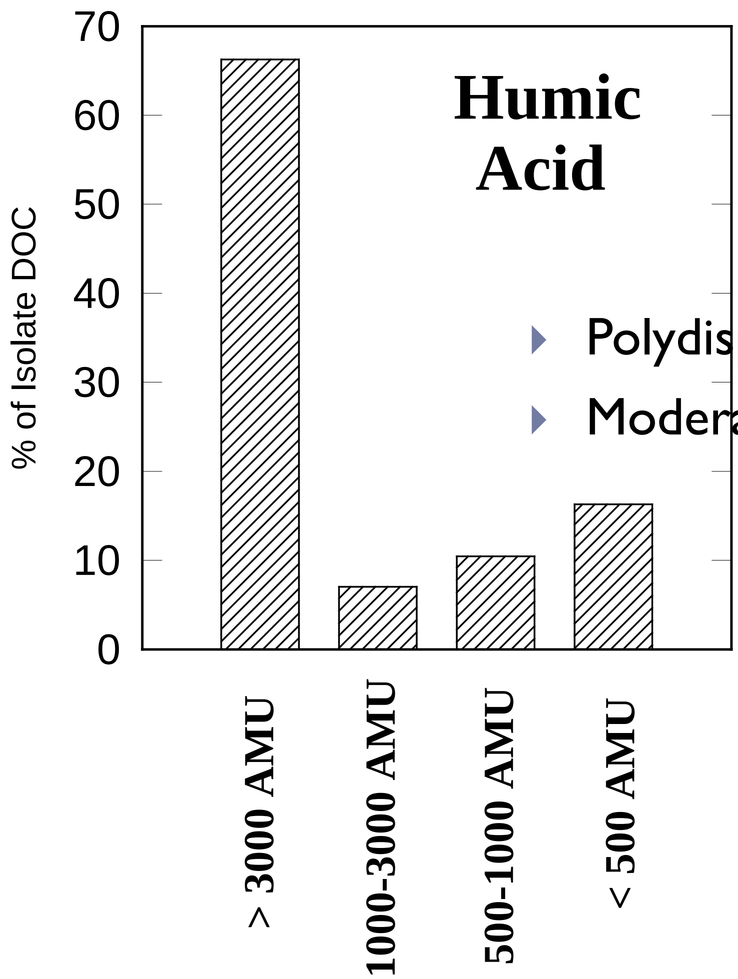
FA=fatty acids; CHO=carbohydrates; AA=amino acids; HC=hydrocarbons (Modified from: Thurman, 1985)

Molecular Size

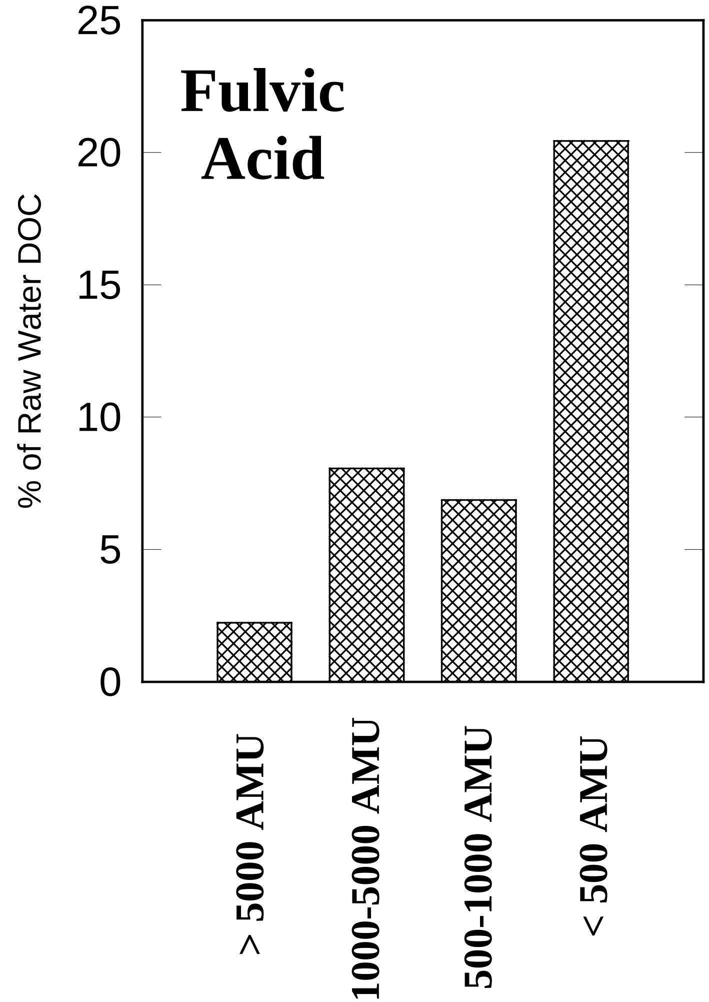
- Ultrafiltration
  - series vs parallel
  - membrane calibration
- Size Exclusion Chromatography
  - HPSEC vs LC
- Others
  - Vapor Pressure Osmometry



Molecular Size: Ultrafiltration



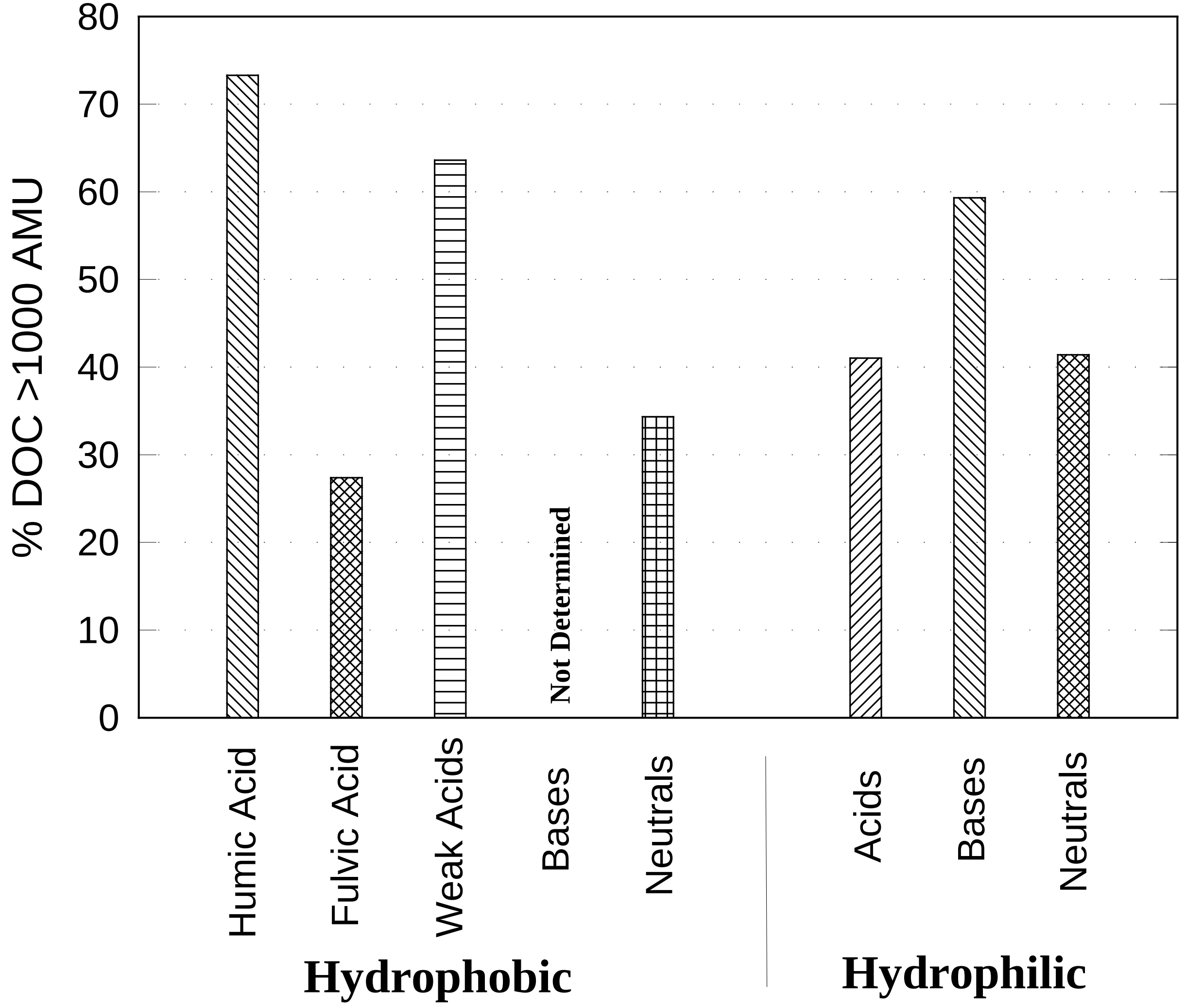
- Polydisperse
- Moderate to large

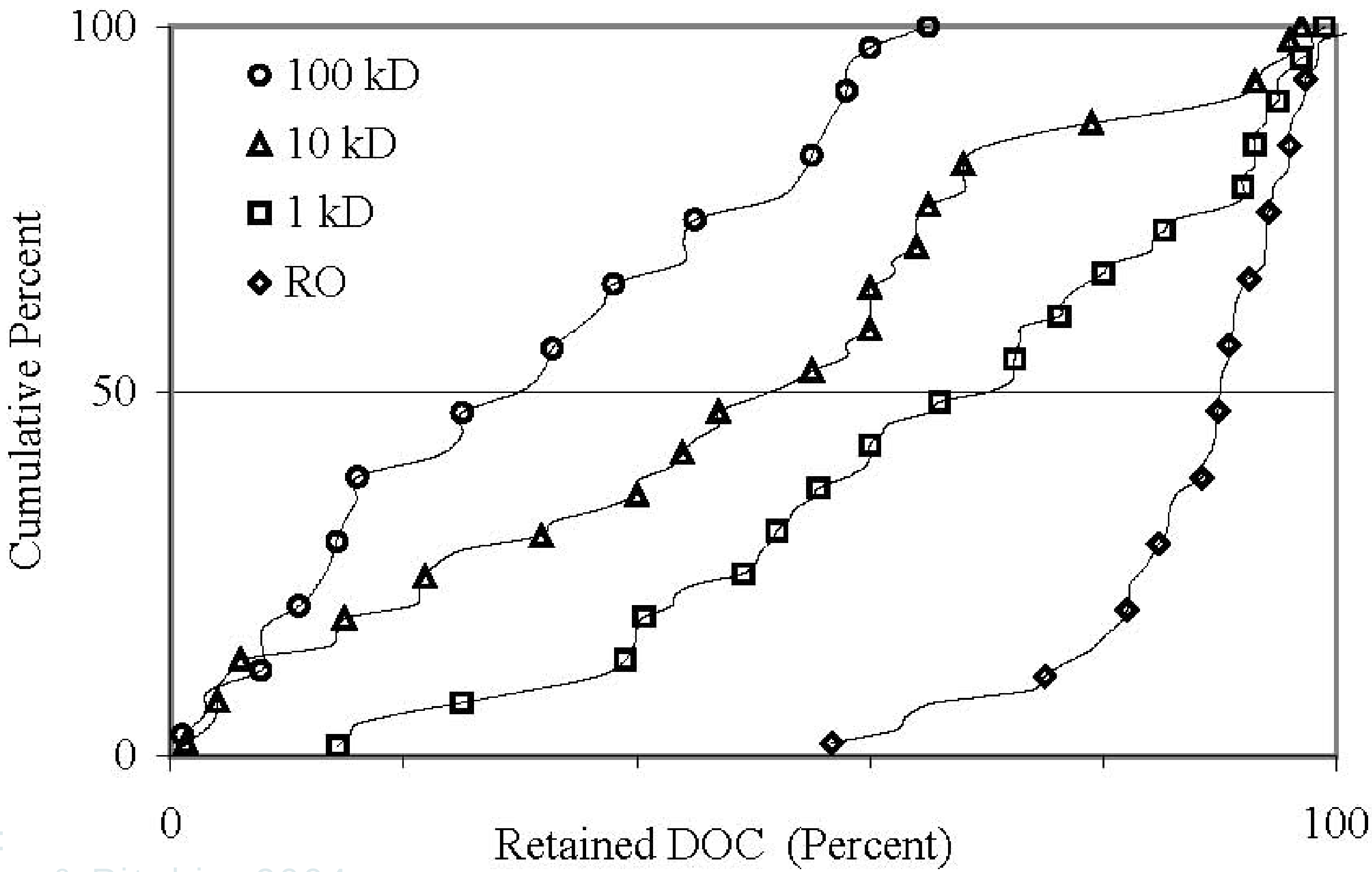


Molecular size: non-humics

Abundance of high-molecular size compounds in Seven Organic Fractions

(from Reckhow et al., 1993)



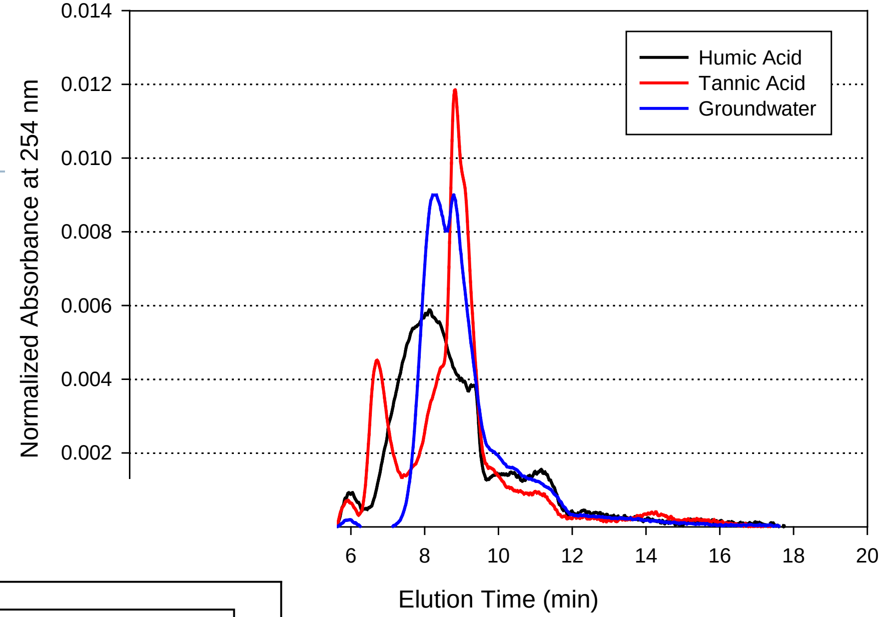


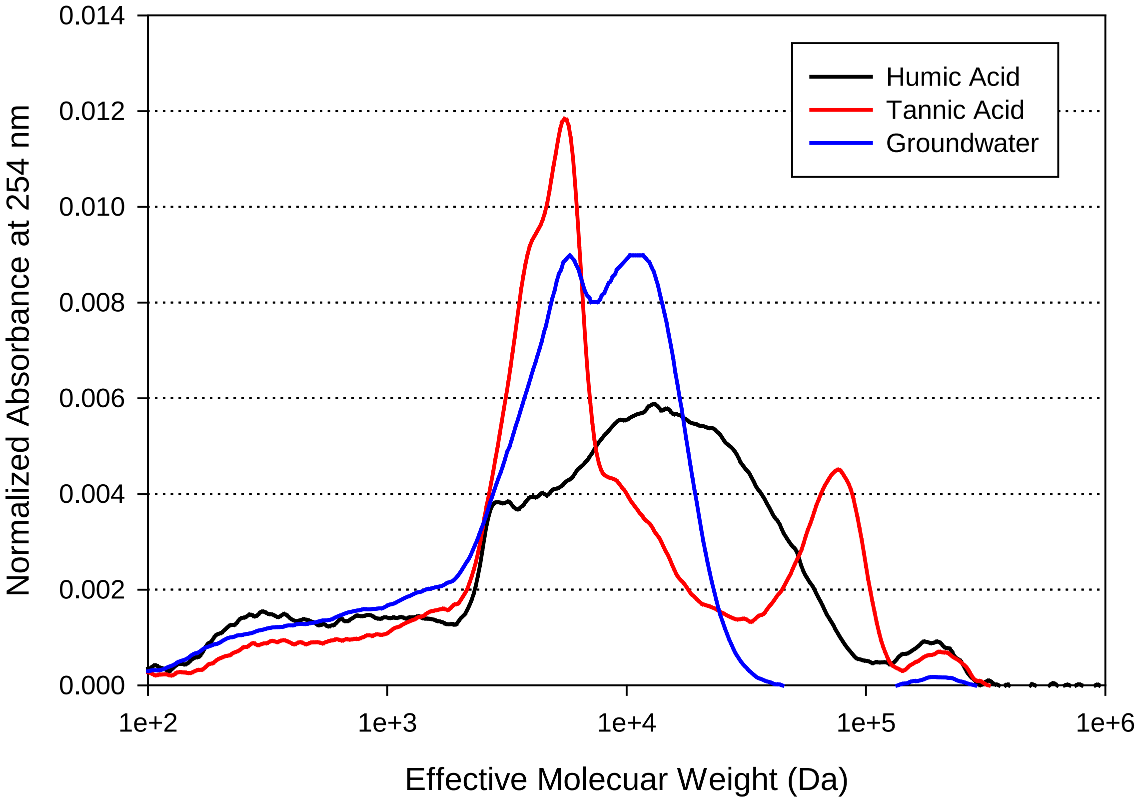
From:
Perdue & Ritchie, 2004

Membrane Cutoff	Obs.	Retained DOC (Percent) Range	Median	Mean	Std. Dev.
100 kD	34	1.0 - 65.0	31.0	31.0	20.0
10 kD	53	1.3 - 97.0	53.0	48.4	28.2
1 kD	68	14.3 - 99.0	71.3	66.2	24.0
Reverse Osmosis	55	56.7 - 104.0	90.1	87.8	9.8

HPSEC

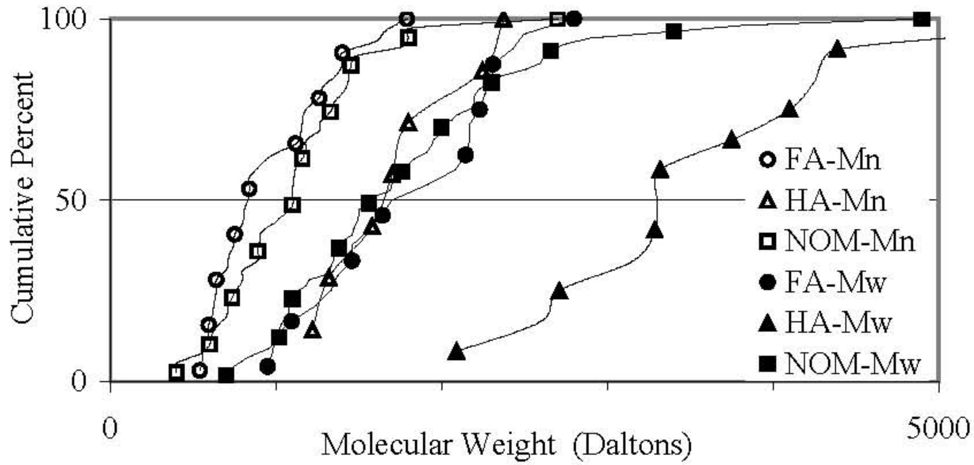
- Effective size
  - UV abs or DOC detection
  - Requires size calibration





- Comparison of HPSEC with FFFF
  - be careful of solute: gel interactions
    - Pelekani et al., 1999 [ES&T, 2807]

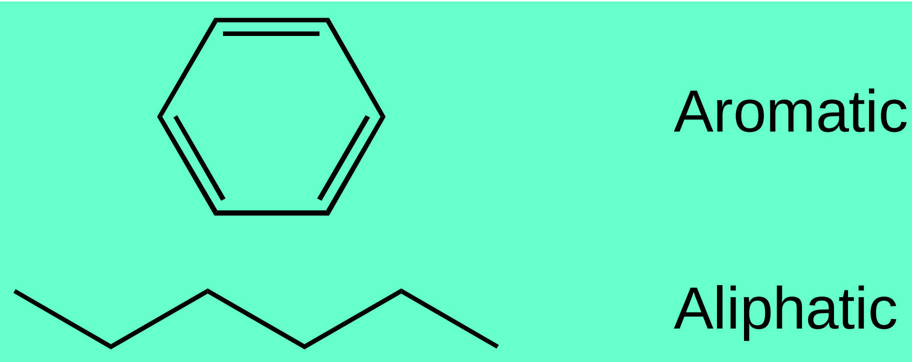
Size: Multiple Methods



Method[a]	Sample	Type[b]	Obs.	Molecular Weight (Daltons) Range	Median	Mean	Std. Dev.
SEC/HPSEC	FA	M_n	11	639 - 1790	1180	1096	362
FFF	FA	M_n	7	980 - 1666	1160	1296	262
CRY/VPO	FA	M_n	14	540 - 900	633	678	118
FFF	HA	M_n	6	1320 - 2374	1750	1837	402
VPO	HA	M_n	1	1220	1220	1220	0
SEC/HPSEC	NOM	M_n	31	400 - 2700	1109	1107	471
FFF	NOM	M_n	7	890 - 1760	910	1133	350
VPO	NOM	M_n	1	614	614	614	0
MALLS	NOM	M_n	2	15,050 - 16,595	15,823	15,823	1092
SEC/HPSEC	FA	M_w	14	980 - 2430	1672	1740	522
FFF	FA	M_w	6	1240 - 2800	1997	1984	612
UV-UCGN	FA	M_w	4	950 - 2260	1815	1710	620
SEC/HPSEC	HA	M_w	2	2600 - 3320	2960	2960	509
FFF	HA	M_w	6	2090 - 4390	3293	3387	808
UV-UCGN	HA	M_w	4	2710 - 6590	4005	4328	1640
SEC/HPSEC	NOM	M_w	37	784 - 2743	1700	1684	530
FFF	NOM	M_w	7	1030 - 4900	1470	2227	1512
DIFF	NOM	M_w	9	700 - 3400	2300	2089	862
MA-UVS	NOM	M_w	4	728 - 1330	982	1005	249
MALLS	NOM	M_w	11	15,000 - 57,800	22,400	25,564	12,607

From:
Perdue & Ritchie, 2004

Aromaticity: ^{13}C-NMR



More reactive with disinfectants
Absorbs UV light

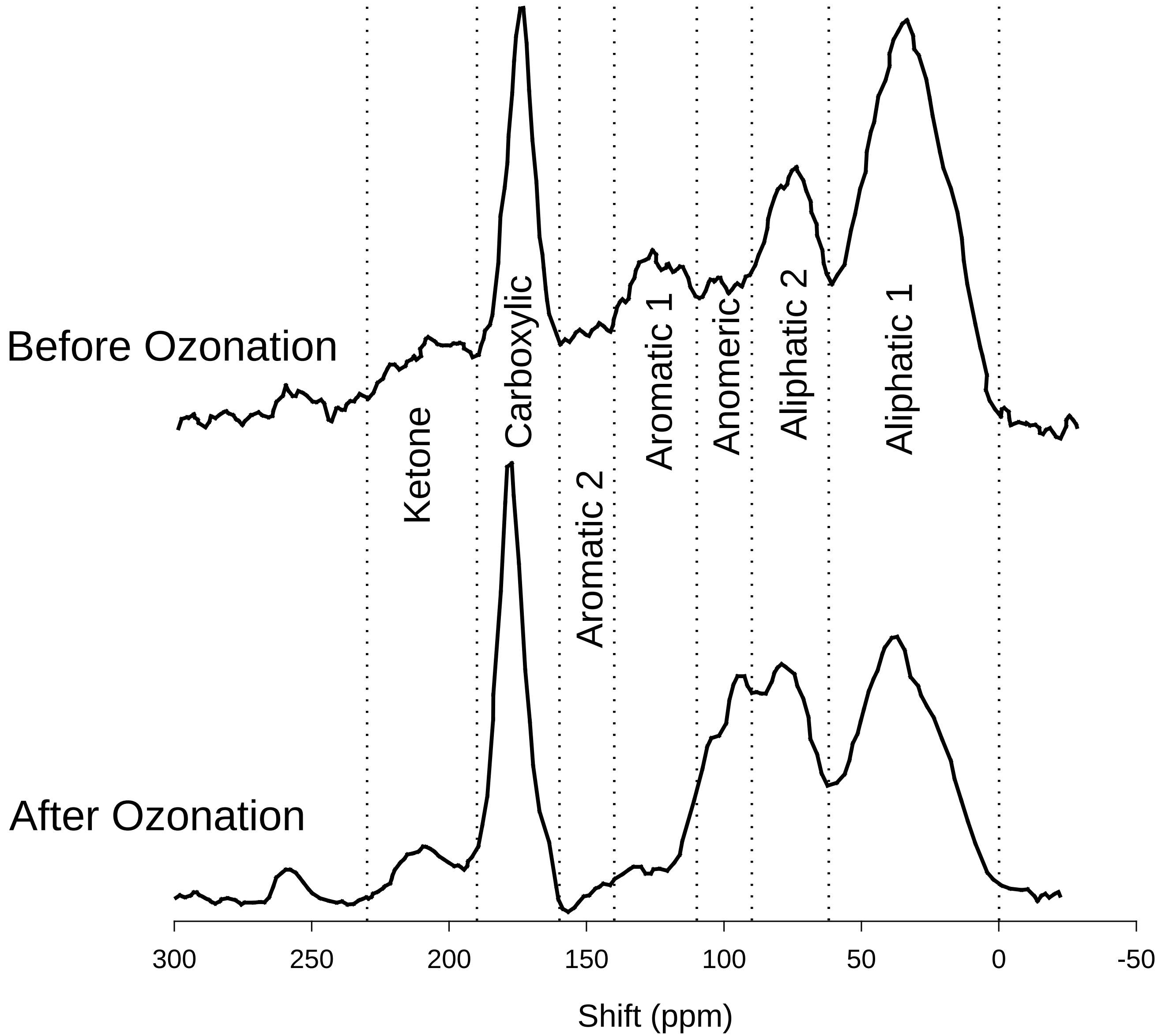
Aromatic and Aliphatic Content of Aquatic Humic Substances

(from Reckhow *et al.*, 1990)

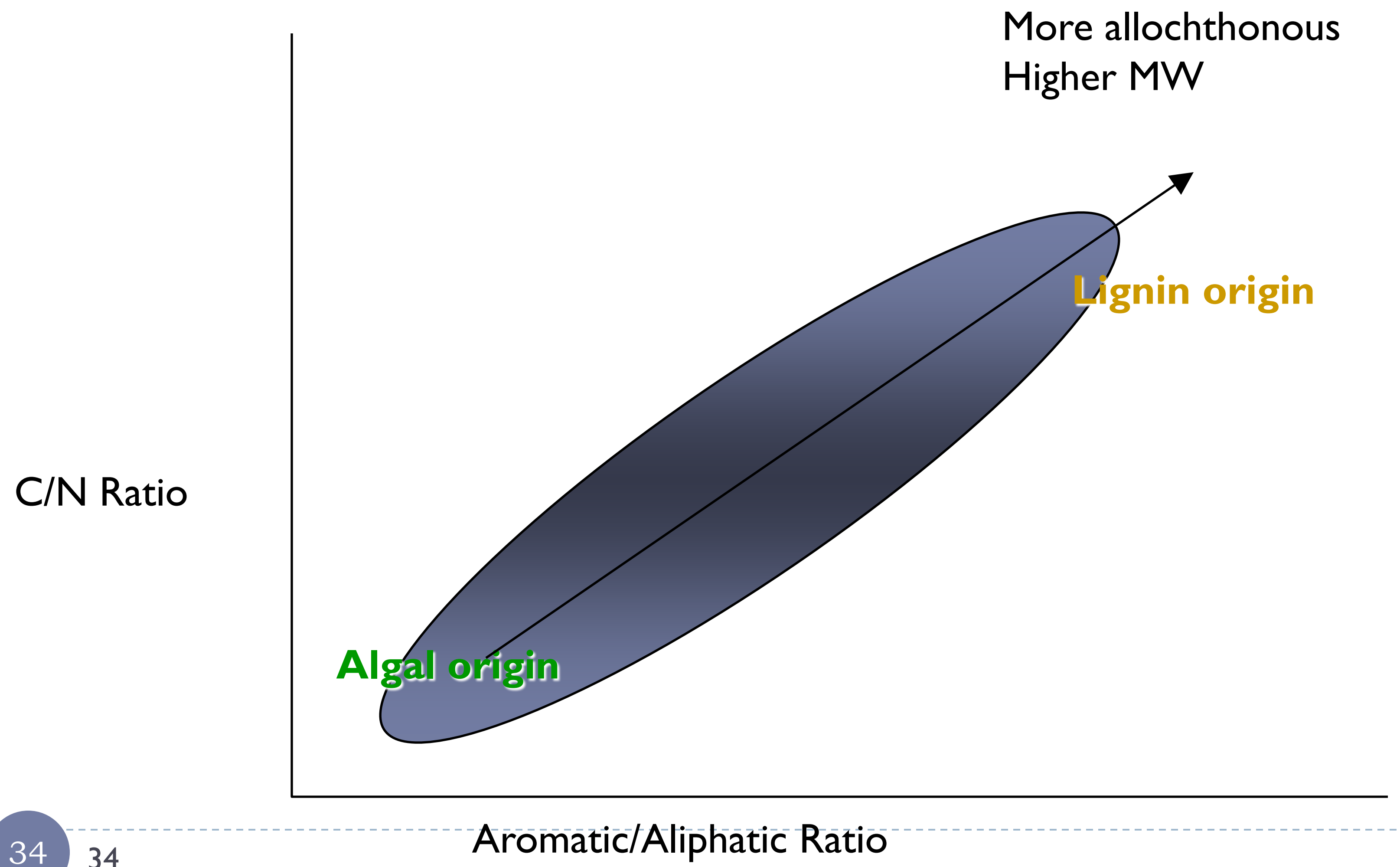
Fraction	Percent Aromatic		Percent Aliphatic	
	Average	Range	Average	Range
Fulvic	17	14-19	59	54-64
Humic	32	30-35	45	38-49

Carbon type: ^{13}C-NMR

Westerhoff et al., 1996



Impact of Origin



Showing “end-members” from McKnight

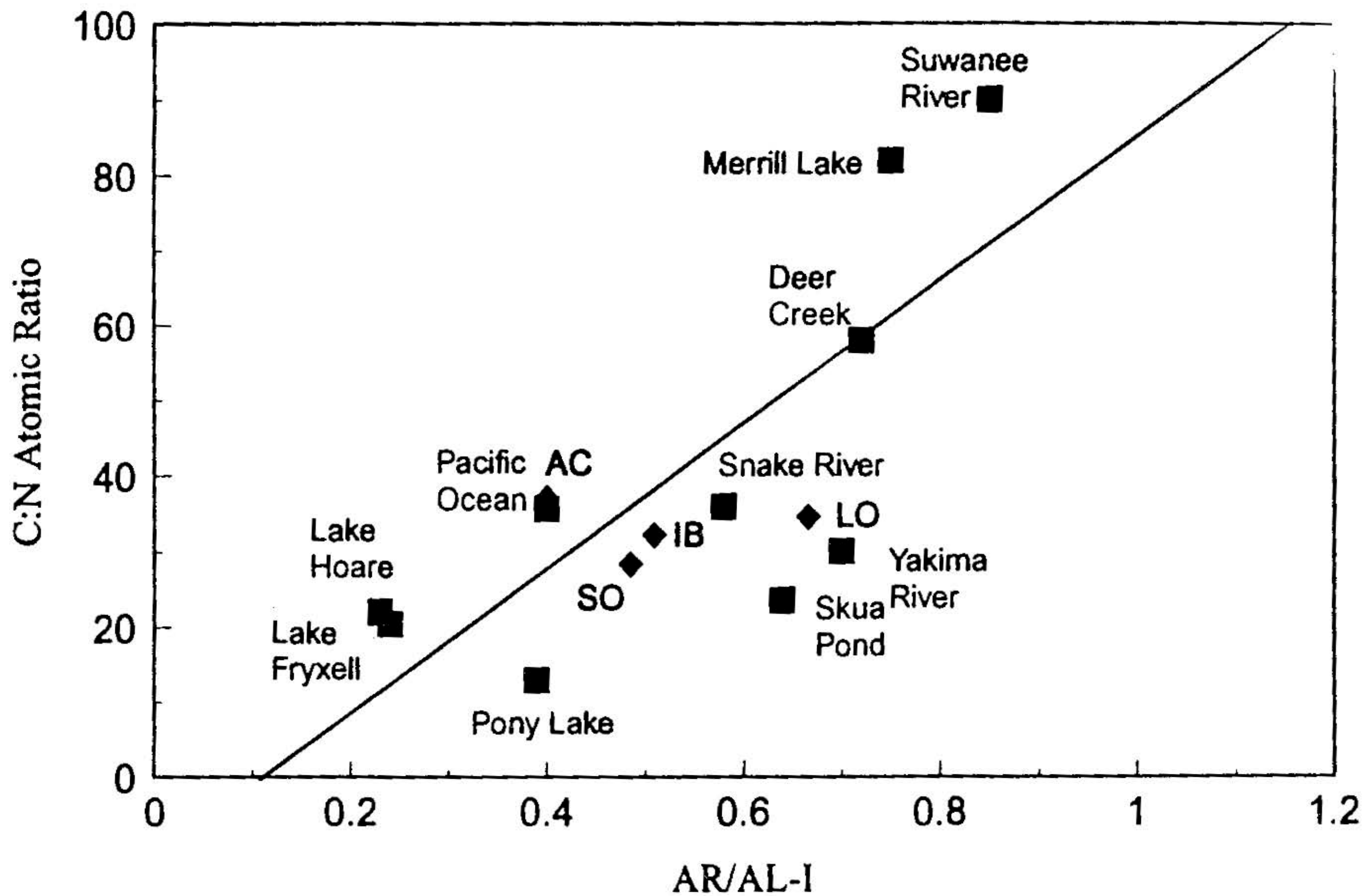
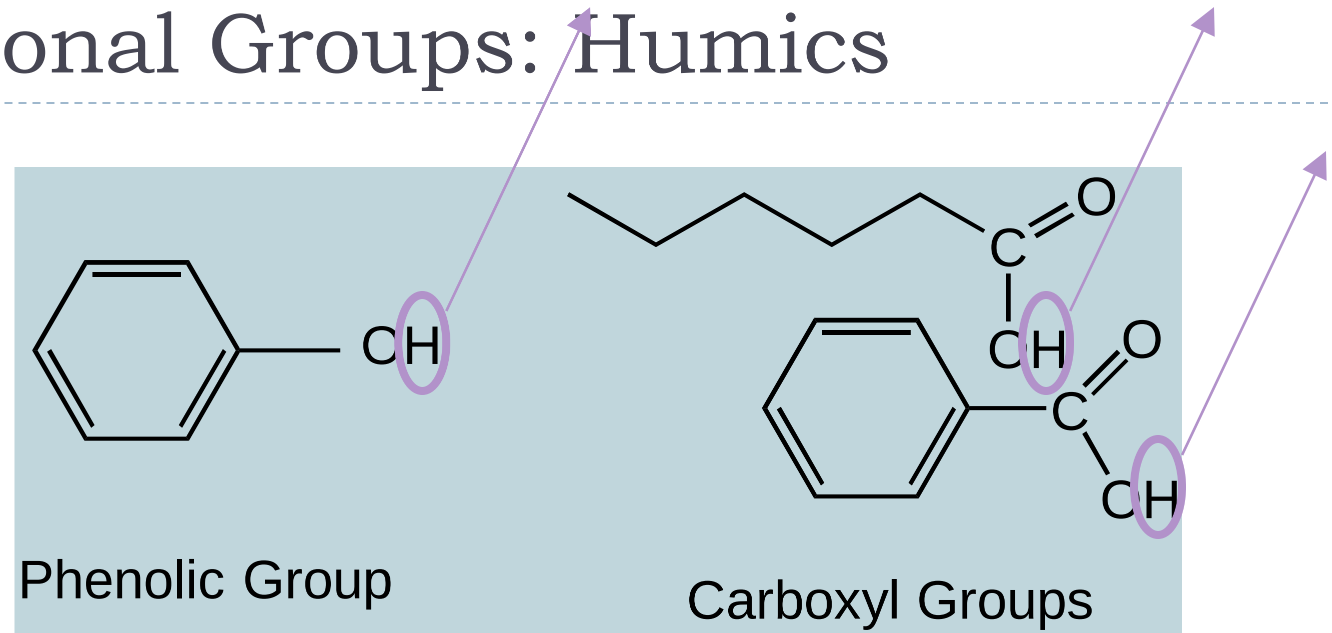


Fig. 1.11. C:N vs. AR:AL-I, showing position of Loch Vale fulvic acids relative to other aquatic fulvic acids. SO Sky Pond Outlet; AC Andrews Creek; IB Icy Brook; LO Loch Outlet. Other fulvic acids are described in McKnight et al. 1994

Functional Groups: Humics



Functional Group Content of Aquatic Humic Substances

(meq/g, After Thurman, 1985)

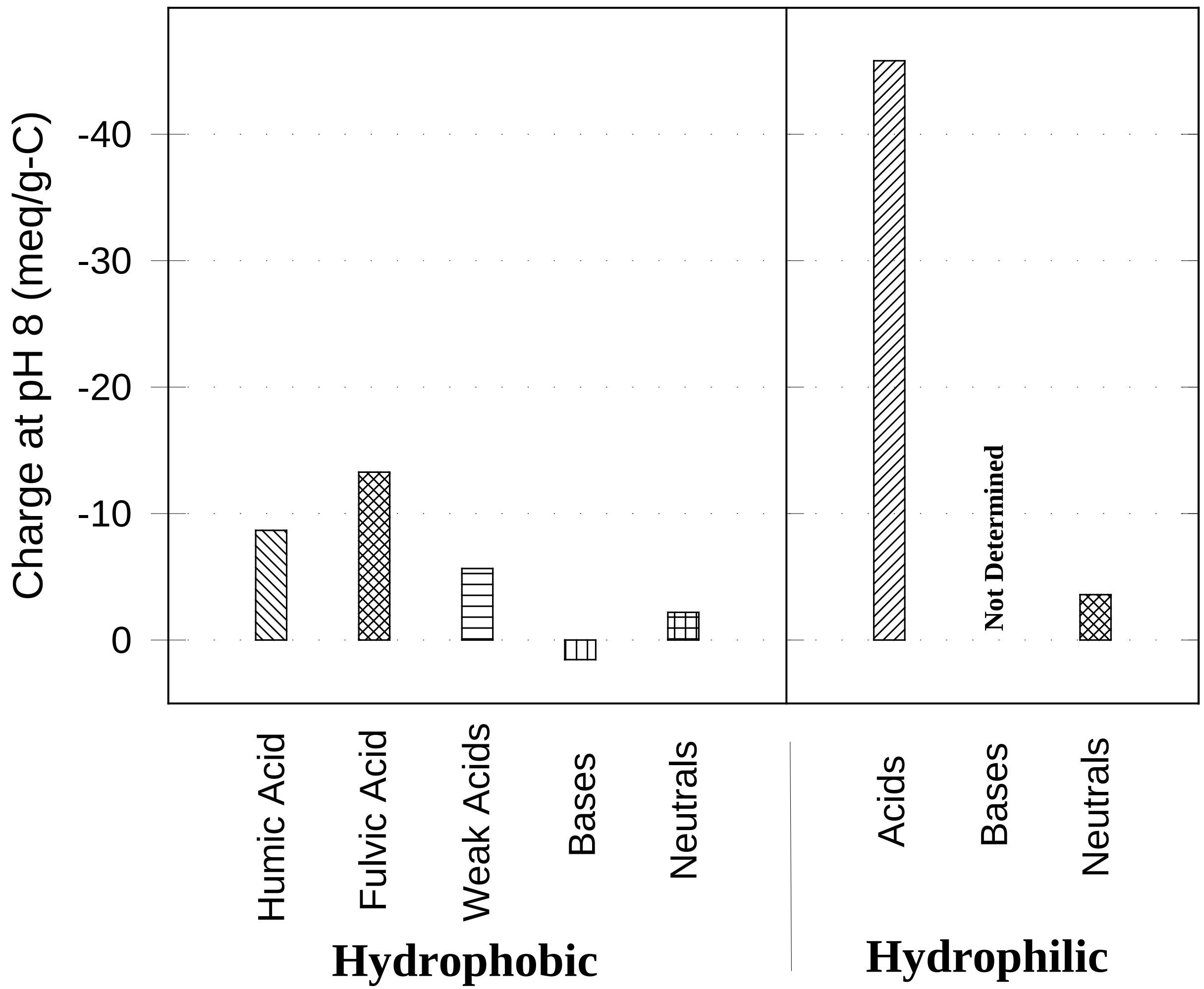
Fraction	Carboxyl	Phenolic
Fulvic	5.5	1.5
Humic	4.0	2.0

- Source of electrical charge; responsible for coagulant demand

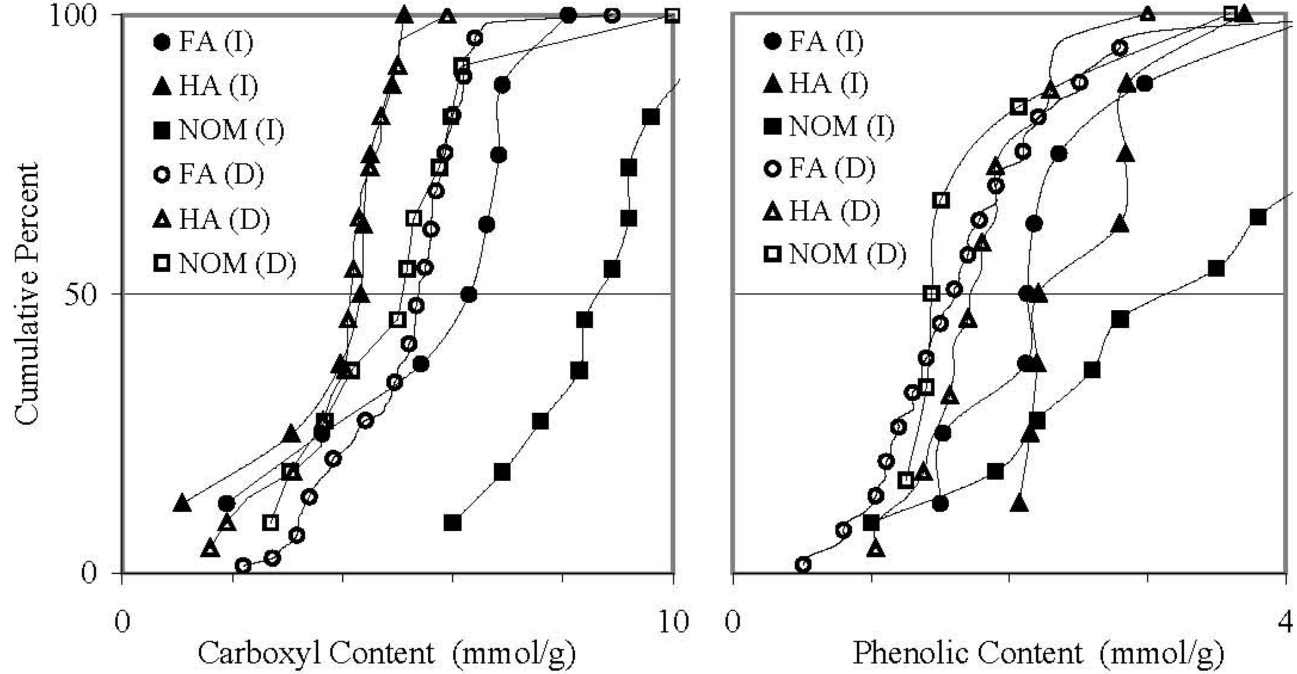
Functional Groups: non-humics

Net Organic Charge on Seven Aquatic Organic Fractions from Forge Pond

(After Reckhow et al., 1993)



Functional Groups

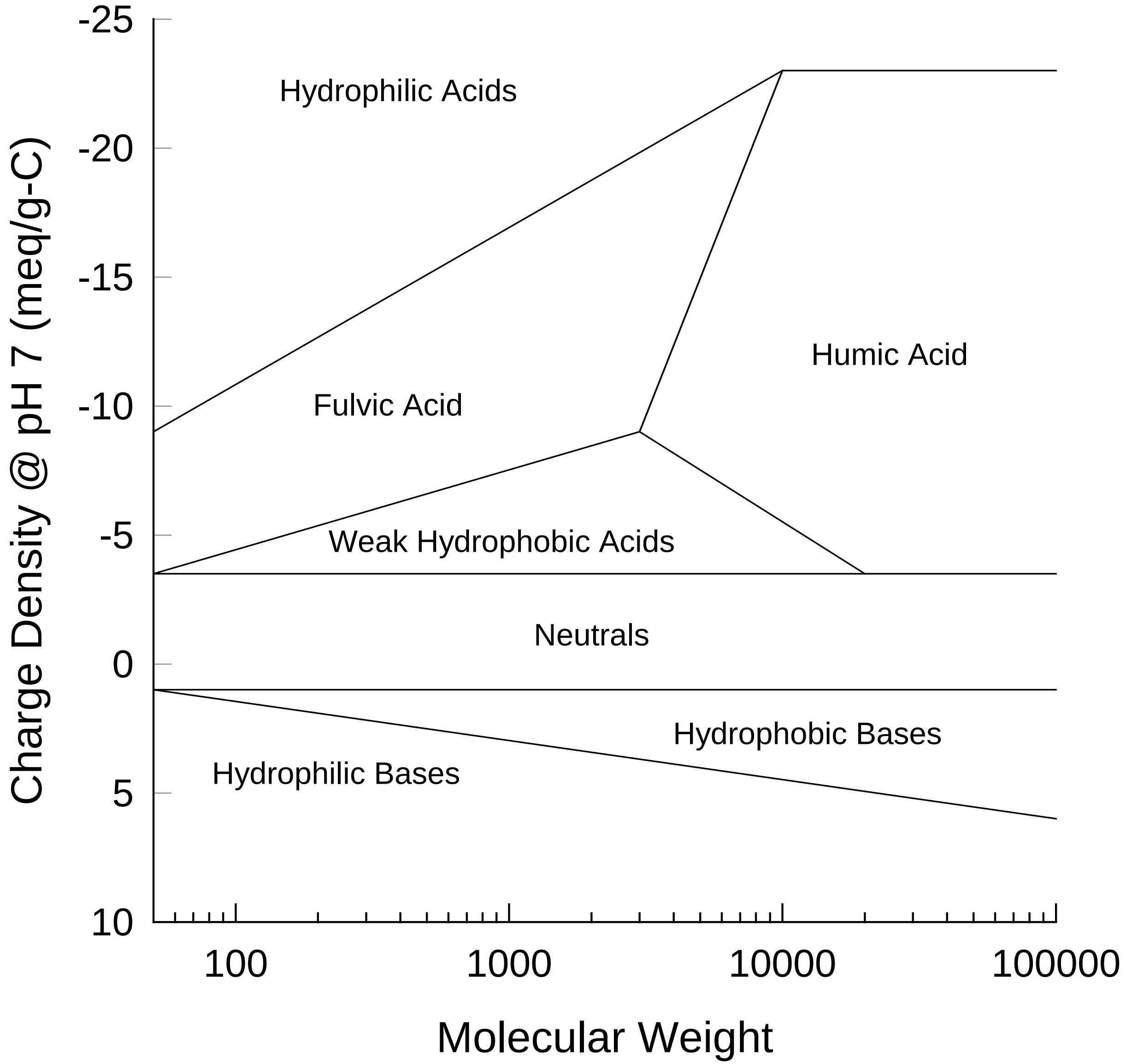


Group (Method)	Sample	Obs.	Acidic Group Content (mmol/g)[a] Range	Median	Mean	Std. Dev.
Carboxyl (Indirect)	FA	8	1.9 - 8.1	6.5	5.7	2.0
	HA	8	1.1 - 5.1	4.4	3.9	1.3
	NOM	11	6.0 - 10.7	8.9	8.7	1.4
Carboxyl (Direct)	FA	73	2.2 - 8.9	5.4	5.1	1.2
	HA	22	1.6 - 5.9	4.2	4.0	1.0
	NOM	11	2.7 - 10.0	5.2	5.2	2.0
Phenolic (Indirect)	FA	8	1.5 - 4.3	2.2	2.4	0.9
	HA	8	2.1 - 3.7	2.5	2.6	0.6
	NOM	11	1.0 - 8.3	3.5	3.6	2.0
Phenolic (Direct)	FA	65	0.5 - 5.1	1.6	1.7	0.8
	HA	22	1.0 - 3.0	1.8	1.8	0.5
	NOM	6	1.3 - 3.6	1.5	1.9	0.9

From:
Perdue & Ritchie, 2004

Size and Charge Relationships for NOM Fractions

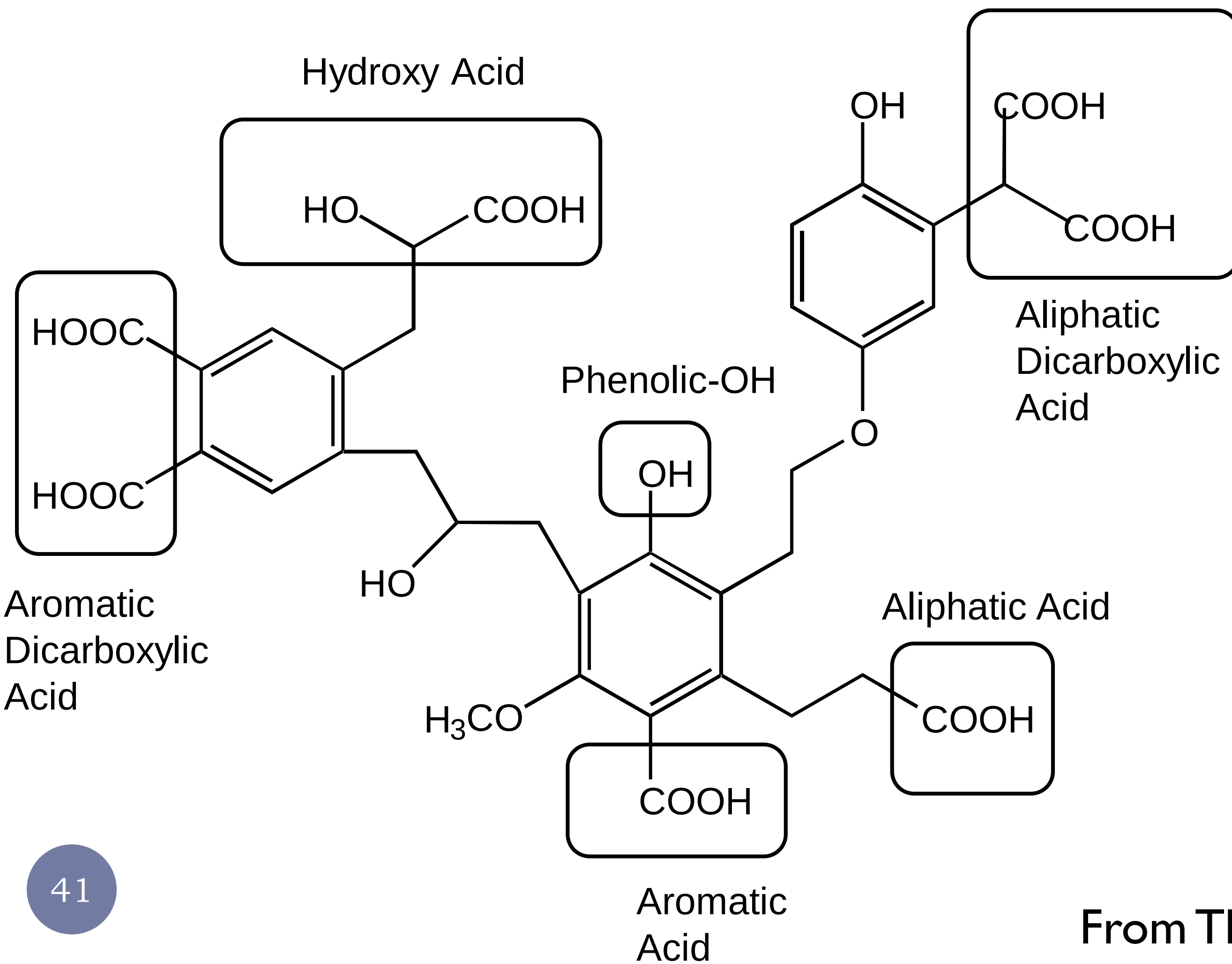
from: Bezbarua and Reckhow, 1995



Functional Groups and Complexation

- Complexation with Coagulants, Major Cations and Heavy Metals
  - soluble complexes
  - surface complexes (insoluble)
- Role of organic structure
  - Enolate > Amine > Azo Compounds > Carboxyl > Ether > Ketone
  - bidentate > monodentate
  - geometry
- Role of metal: the Irving-Williams series:
  - Fe^{+3}> Al^{+3}> Pb^{+2}> Hg^{+2}> Cu^{+2}> Ni^{+2}> Zn^{+2}> Co^{+2}> Fe^{+2}> Mn^{+2}> Cd^{+2}> Ca^{+2}> Mg^{+2}

An Aquatic Humic "Structure"

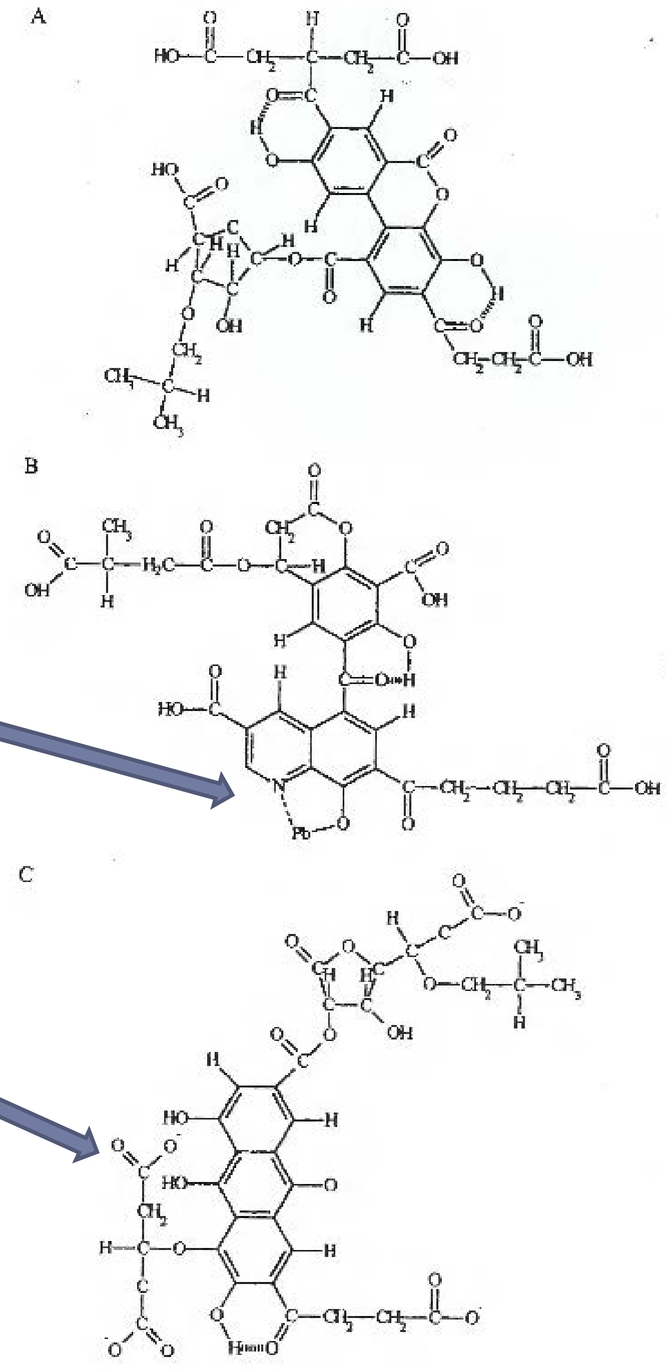


- **Features**
  - Aromatic rings
    - Reactive with oxidants
  - Aliphatic carbon chains
  - Many oxygenated groups that can bind with coagulants
    - Phenolic -OH
    - Aliphatic -OH
    - Carboxylic (COOH)

From Thurman, 1985

Other Concepts

- From Suwanee River FA characterization
  - A. Simple view
  - B. With an N (anthranillic acid – type)
  - C. Containing a semiquinone free radical



Averett et al., 1988

- To next lecture