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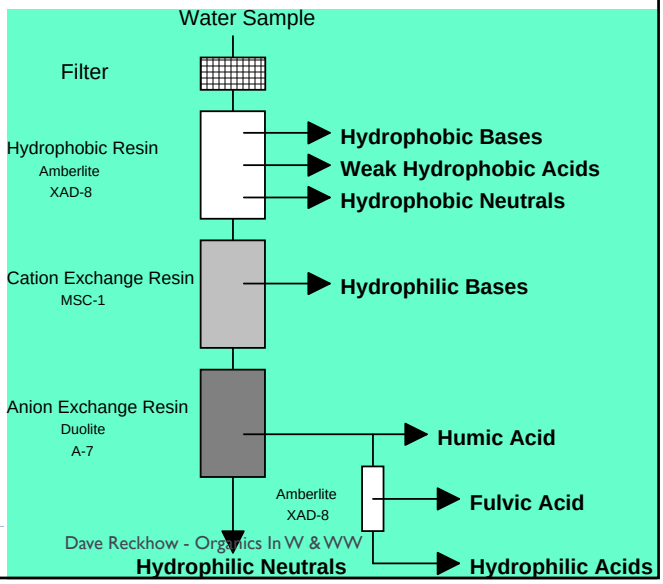
CEE 697z
Organic Compounds in Water and Wastewater

Isolation of NOM

Lecture #3

A USGS Preparative-based method

Leenheer, J.A. and Noyes, T.I. (1984) *A Filtration and Column-Adsorption System for Onsite Concentration and Fractionation of Organic Substances from Large Volumes of Water*, U.S. Geological Survey Water Supply Paper 2230, U.S. Government Printing Office, Washington, D.C.



Elemental Composition: Humics

Elemental Composition of Aquatic Humic Substances

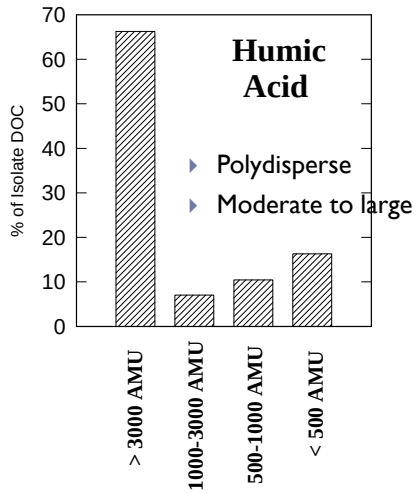
(average of 15 riverine samples, after Thurman, 1985)

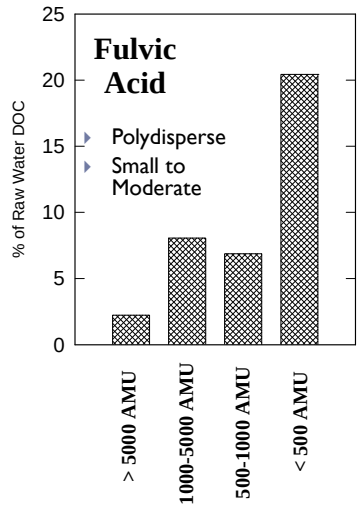
Fraction	C	H	O	N	P	S	Ash
Fulvic	51.9	5.0	40.3	1.1	0.2	0.6	1.5
Humic	50.0	4.7	39.6	2.0			5.0

High oxygen content
FA and HA Similar, except:

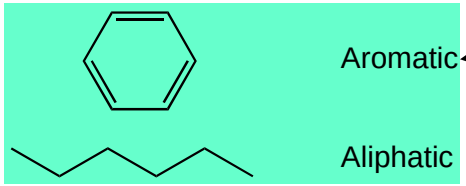
- humics tend to have more N

Molecular Size: Ultrafiltration





Aromaticity: ^{13}C-NMR



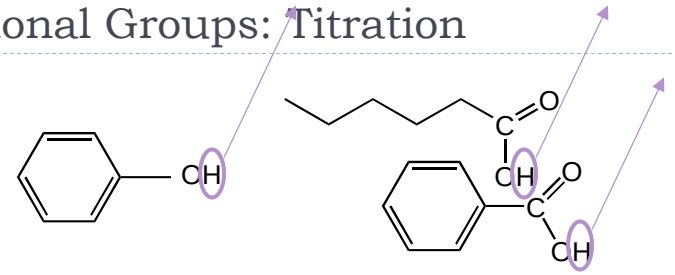
More reactive with disinfectants
Absorbs UV light

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

Functional Groups: Titration



Phenolic Group

Carboxyl Groups

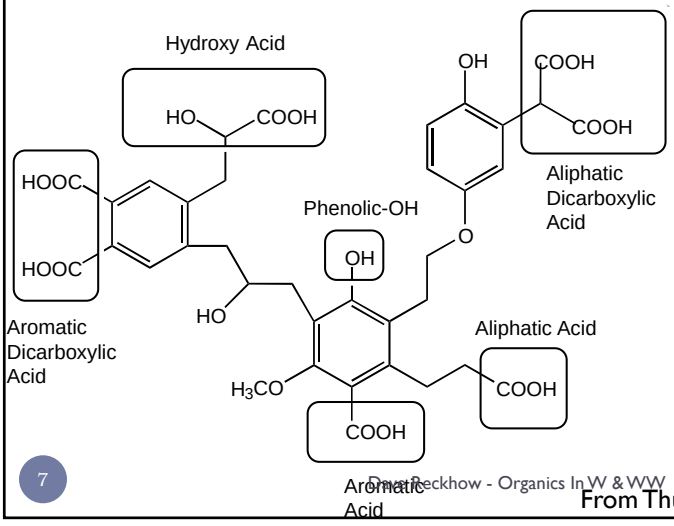
Functional Group Content of Aquatic Humic Substances

(meq/g-C, After Thurman, 1985)

Fraction	Carboxyl	Phenolic
Fulvic	11	3
Humic	8	4

Source of electrical charge; responsible for coagulant demand

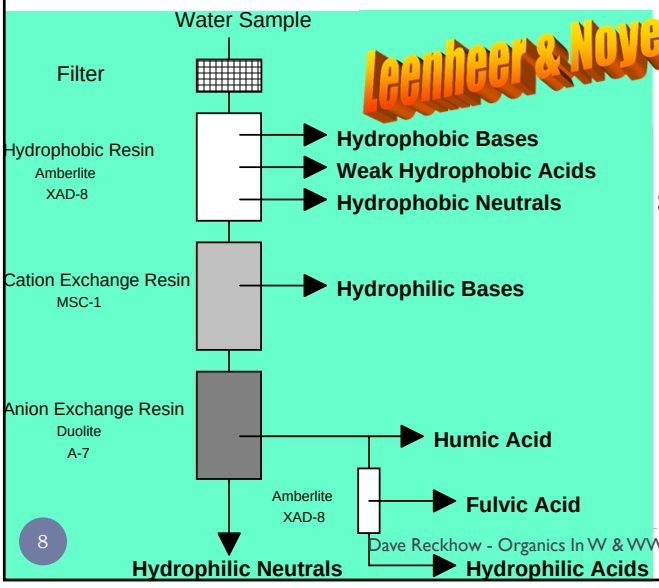
An Aquatic Humic "Structure"



- 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

The Humics and Non-humics: Comprehensive NOM Fractionation

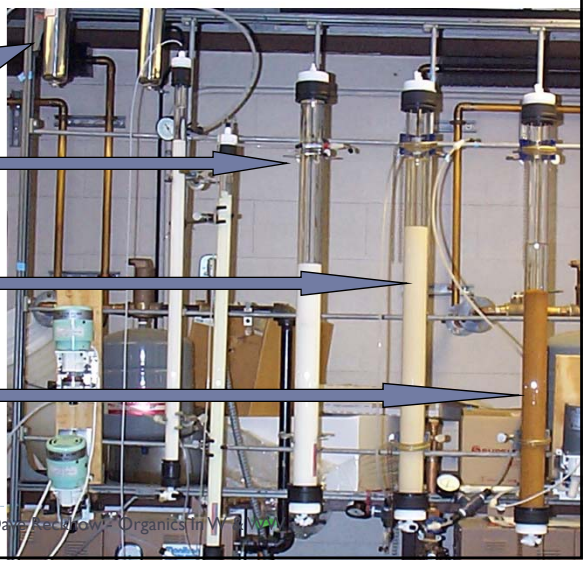


USGS method adapted by water industry

- Idea: separate NOM into groups of compound of similar properties

UMass Lab setup

- Pre-filters
- Hydrophobic resin
  - XAD-8
- Cation Exchanger
  - MSC-1
- Anion Exchanger
  - A-7



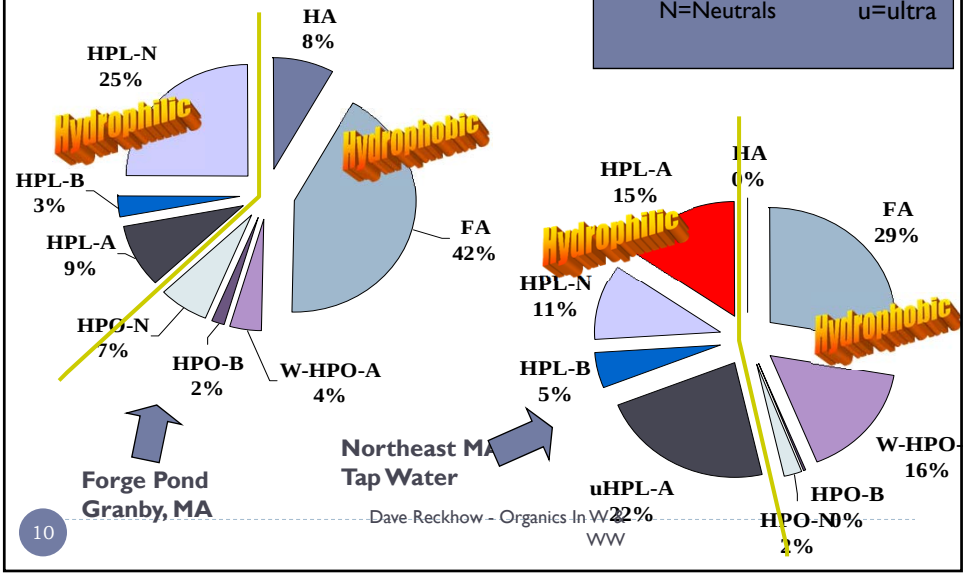
9

NOM Fractions: Mass Balance

HPL=Hydrophilic
HPO=Hydrophobic

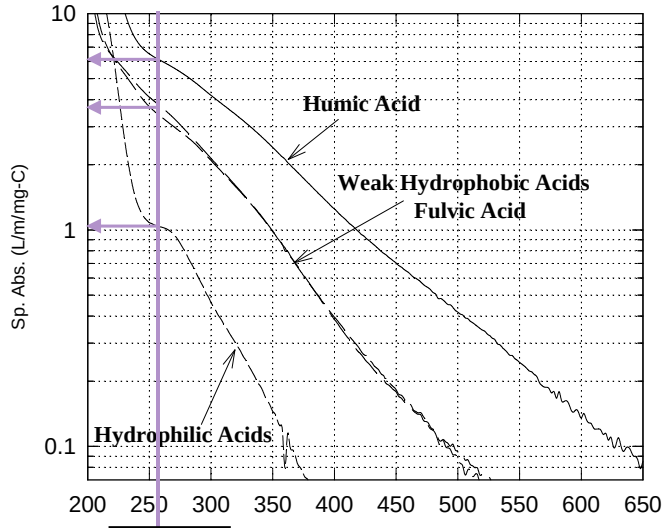
A=Acids
B=Bases
N=Neutrals

W=Weak
u=ultra



10

Absorbance of Acid Fractions

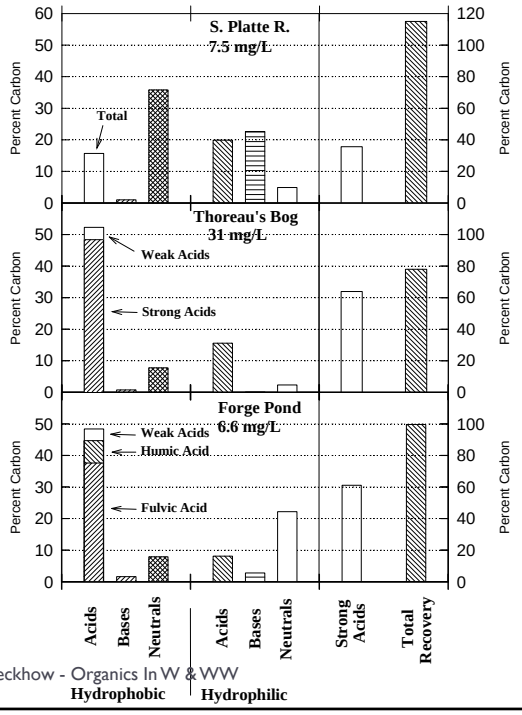


Same DOC

Dave Reckhow - Organics In W & WW

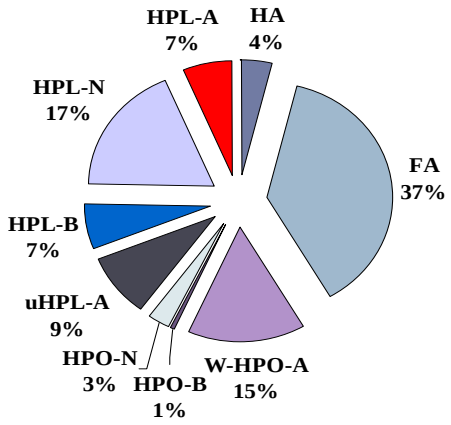
Different Water Types

- South Platte River (Leenheer)
- Thoreau's Bog (Leenheer)
- Forge Pond (Bose & Reckhow)

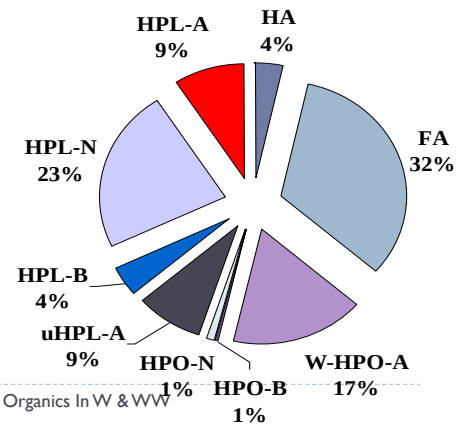


Dave Reckhow - Organics In W & WW

NOM Fractions: Seasonal Effects

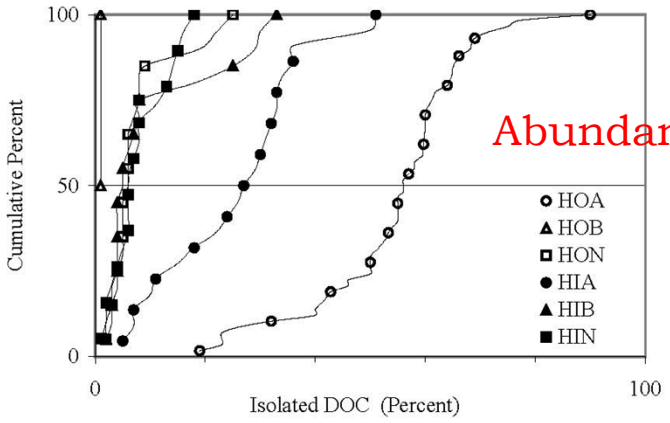


New England Reservoir
Spring



New England Reservoir
Fall

Dave Reckhow - Organics In W & WW



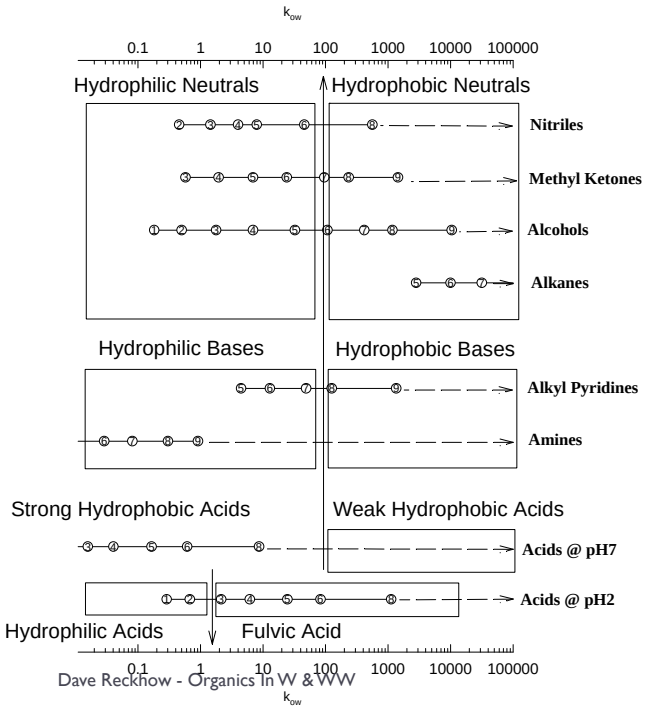
Abundance

From:
Perdue & Ritchie, 2004

Fraction	Obs.	Isolated DOC (Percent) Range	Median	Mean	Std. Dev.
Hydrophobic Acids (HOA)	58	19.0 - 90.0	56.0	54.4	13.8
Hydrophobic Bases (HOB)	2	1.0 - 1.0	1.0	1.0	0
Hydrophobic Neutrals (HON)	20	2.0 - 25.0	6.0	7.8	6.5
Hydrophilic Acids (HIA)	22	5.0 - 51.0	28.0	25.8	12.9
Hydrophilic Bases (HIB)	20	2.0 - 33.0	5.0	10.3	10.4
Hydrophilic Neutrals (HIN)	19	1.0 - 18.0	6.0	7.9	5.1

Chemical Interpretations

- May be related to known Octanol:water partition coefficients



Other Qualitative Interpretations

Fraction		Composition
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 (C12) 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
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

Based on: Leenheer and Noyes, 1984; Leenheer et al., 1982; and others

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

- To next lecture