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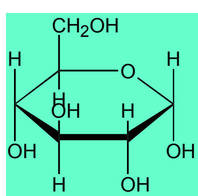
CEE 697z
Organic Compounds in Water and Wastewater

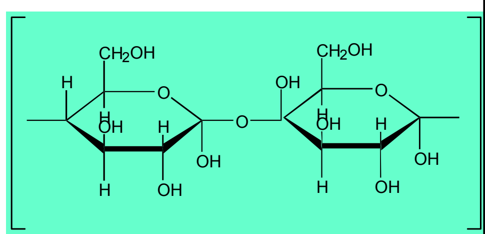
Origins of NOM II

Lecture #5

Carbohydrates

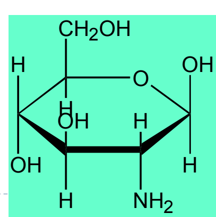
- empirical formula: $C_x(H_2O)_y$





Glucose (monosaccharide) Cellulose (polysaccharide)

Glucosamine (amino sugar)



Carbohydrates, cont.

- Nomenclature
  - Monosaccharide: 1 simple sugar
    - 1% of DOC
  - Oligosaccharide: ≤10 simple sugars
  - Polysaccharide: > 10 simple sugars
    - 5% of DOC
- Special interest in distribution systems
  - Food for microbial regrowth
  - Major constituents of:
    - soluble metabolic byproducts
    - biofilms

Carbohydrates, cont.

- Function in plants
  - Structural – cell walls
    - Cellulose (~10,000 D-glucose units)
      - Most abundant natural organic compound
      - Mostly in higher plants; some algae have none
    - Hemicelluloses (50-2000 monosaccharides of many types)
      - Forms a matrix around cellulose fibers in cell walls
    - Chitin (N-acetyl-D-glucosamine units)
      - Second most abundant natural organic (~tied with lignin)
      - Role of cellulose in most fungi, some algae & arthropods
    - Murein or "peptidoglycan", a major group of Acylheteropolysaccharides
      - N-acetyl-D-glucosamine & N-acetylmuiramic acid cross linked by AA chains
      - Dominant in Eubacteria: up to 75% of bacterial dry mass
  - Energy – polysaccharides
    - Starch in plants (80% amylopectin, 20% amylose)
  - Anti-dessicants

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Carbohydrates, cont.

Algae etc.,
Heteropolysaccharides
Nitrogen-containing

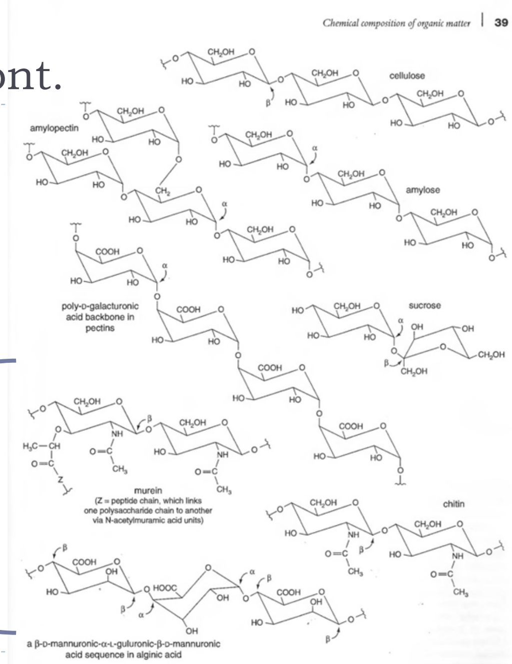

Fig. 2.9 Some important carbohydrates (showing configuration at C-1 in monosaccharide units).

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Carbohydrates, cont.

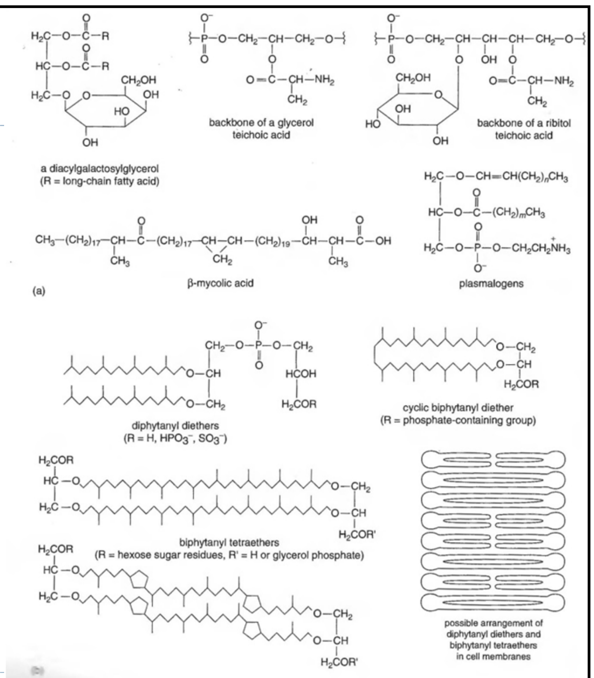

Fig. 2.15 (a) Examples of lipids in the membranes and cell walls of eubacteria. (b) Phytanyl ether lipids in archaebacterial cell membranes.

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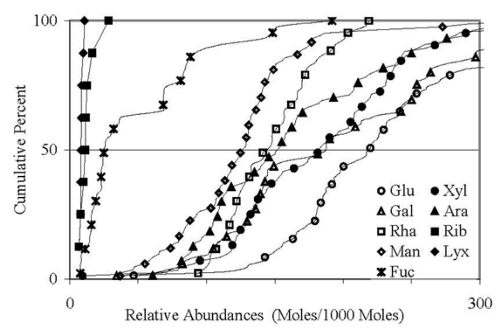
Acylheteropolysaccharides (APS)

- 10-35% of river and lake water DOC
- Produced by algae in fresh and salt waters
- Similar to structural polysaccharides?
- Comprised of a nearly fixed ratio of simple sugars, acetate and lipids
- Refractory like humic substances

Sugars in Natural Waters



Sugar	Obs.	Relative Abundances (Moles/1000 Moles) Range	Median	Mean	Std. Dev.
Glucose (Glu)	71	47 - 591	220	264	140
Galactose (Gal)	85	35 - 875	188	204	113
Rhamnose (Rha)	43	94 - 219	147	147	33
Mannose (Man)	84	37 - 357	127	126	51
Fucose (Fuc)	43	8 - 192	26	50	46
Xylose (Xyl)	84	9 - 400	183	184	67
Arabinose (Ara)	87	61 - 455	153	167	77
Ribose (Rib)	8	7 - 28	12	13	7
Lyxose (Lyx)	8	7 - 11	8	9	1

	Obs.	Concentration Range	Median	Mean	Std. Dev.
Total Sugars (μmol L^{-1})	104	0.08 - 20.0	2.6	3.1	2.7
% DOC as Sugars	95	0.08 - 35.1	3.0	7.1	8.4

From:
Perdue & Ritchie, 2004

Fatty Acids

At neutral pH's most lose H^+

CH_3-COO^-

- maybe 4% of DOC
- other mixed acids may account for 2%

H-$COOH$ Formic Acid

CH_3-$COOH$ Acetic Acid

CH_3-CH_2-$COOH$ Propionic Acid

CH_3-CH_2-CH_2-$COOH$ Butyric Acid

H_3-CH_2-CH_2-CH_2-$COOH$ Valeric Acid

Common Volatile Fatty Acids in Natural Waters

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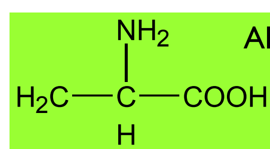
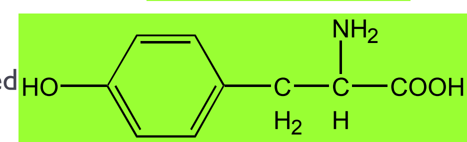
Amino Acids and Proteins

- Simple Amino Acids
  - some may form THMs and HANs
- Proteins
  - much larger, comprised many AAs



Alanine



Tyrosine

- Special interests in DWT
  - nutrients for bacterial regrowth
  - role in chlorine decay and DBP formation

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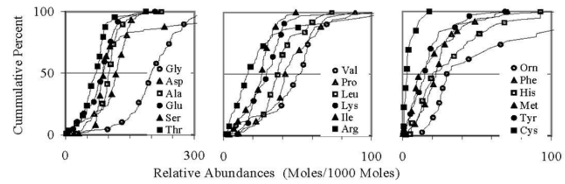
Amino Acids



Amino Acid	THAA[a]	TFAA[a]	Relative Abundances (Moles/1000 Moles) Range	Median	Mean	Std. Dev.
Glycine (Glu)	69	19	26 - 450	200	206	64
Aspartic (Asp)	69	19	20 - 212	117	113	38
Alanine (Ala)	69	18	4 - 223	102	98	37
Glutamic (Glu)	69	17	14 - 208	88	84	36
Serine (Ser)	69	19	31 - 483	88	126	94
Threonine (Thr)	69	19	2 - 187	73	70	33
Valine (Val)	69	16	2 - 145	52	49	24
Proline (Pro)	50	2	10 - 89	42	45	17
Leucine (Leu)	68	19	3 - 73	37	38	14
Ornithine (Orn)	25	9	13 - 190	31	55	45
Lysine (Lys)	69	9	9 - 149	29	31	18
Isoleucine (Ile)	67	19	4 - 49	26	24	10
Phenylalanine (Phe)	68	19	2 - 70	23	24	14
Histidine (His)	56	18	5 - 93	20	28	20
Arginine (Arg)	52	15	2 - 117	17	26	25
Tyrosine (Tyr)	61	19	0.5 - 69	15	17	14
Methionine (Met)	60	16	0.2 - 108	12	21	20
Cysteine (Cys)	13	0	1 - 18	3	5	5

	Obs.	Concentration Range	Median	Mean	Std. Dev.
THAA (μmol L^{-1})	51	0.12 - 23.2	1.3	4.1	6.2
TFAA (μmol L^{-1})	21	0.05 - 1.8	0.3	0.6	0.5
% DOC as THAA	59	0.42 - 10.4	1.8	2.2	1.8
% DOC as TFAA	14	0.02 - 1.2	0.1	0.3	0.4

From:
Perdue & Ritchie, 2004

Terpenes and Terpenoids

- The **terpenoids**, sometimes called **isoprenoids**, are a large and diverse class of naturally occurring organics similar to terpenes, derived from five-carbon isoprene units assembled and modified in thousands of ways.
  - Terpenoids can be thought of as modified terpenes, wherein methyl groups have been moved or removed, or oxygen atoms added.
- Plant terpenoids are used extensively for their aromatic qualities. They play a role in traditional herbal remedies and are under investigation for antibacterial, antineoplastic, and other pharmaceutical functions. Terpenoids contribute to the scent of eucalyptus, the flavors of cinnamon, cloves, and ginger, the yellow color in sunflowers, and the red color in tomatoes.
- Terpenoids can be classified according to the number of isoprene units used:
  - Hemiterpenoids, 1 isoprene unit (5 carbons)
  - Monoterpenoids, 2 isoprene units (10C)
  - Sesquiterpenoids, 3 isoprene units (15C)
  - Diterpenoids, 4 isoprene units (20C) (e.g. ginkgolides)
  - Sesterterpenoids, 5 isoprene units (25C)
  - Triterpenoids, 6 isoprene units (30C) (e.g. sterols)
  - Tetraterpenoids, 8 isoprene units (40C) (e.g. carotenoids)
  - Polyterpenoid with a larger number of isoprene units

From Wikipedia

Terpenoids

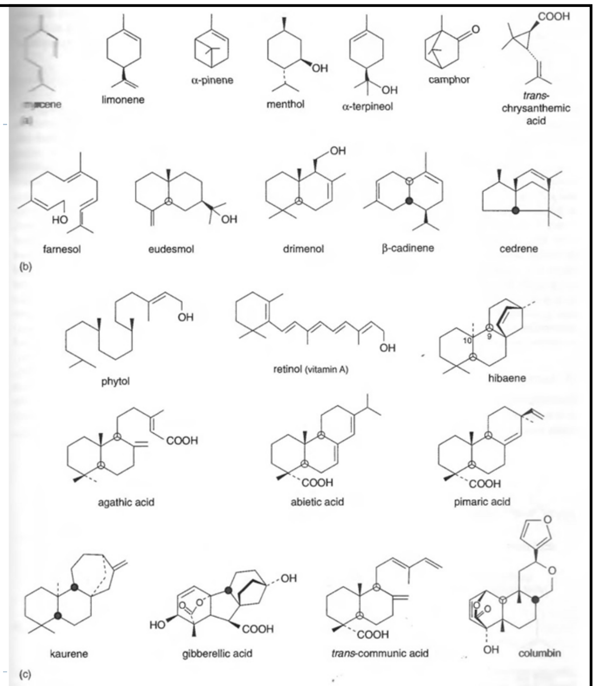


Fig. 2.17 Examples of (a) monoterpenoids, (b) sesquiterpenoids and (c) diterpenoids.

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Terpenoids, cont.

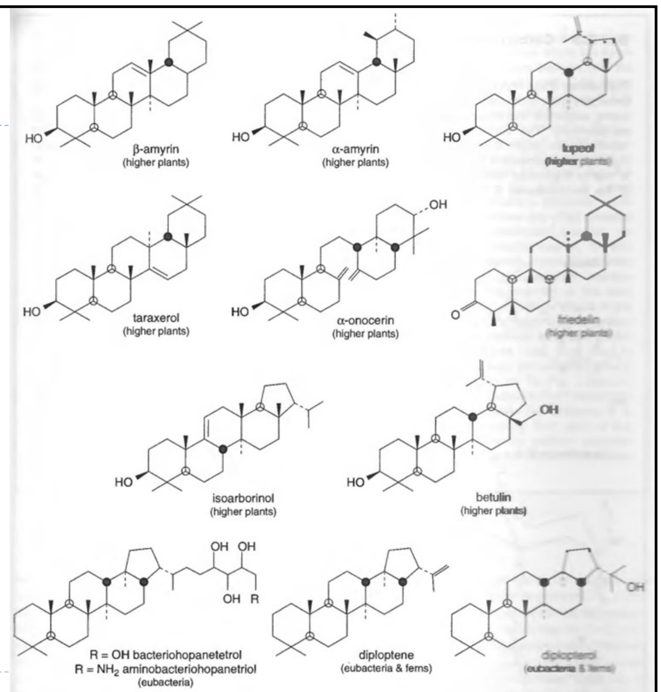

Fig. 2.19 Some geochemically important polycyclic triterpenoids and their major sources.

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Iron Complexation

Iron is a vital component of the proteins involved in photosynthesis, respiration and nitrogen fixation, but under oxic conditions it is predominantly found in its extremely low solubility Fe(III) form and so is not readily available for uptake by organisms. Unlike anoxic environments, in which soluble Fe(II) is generally abundant, the well oxygenated surface waters of the open oceans can contain as little as 10^{-8} g l^{-1} of

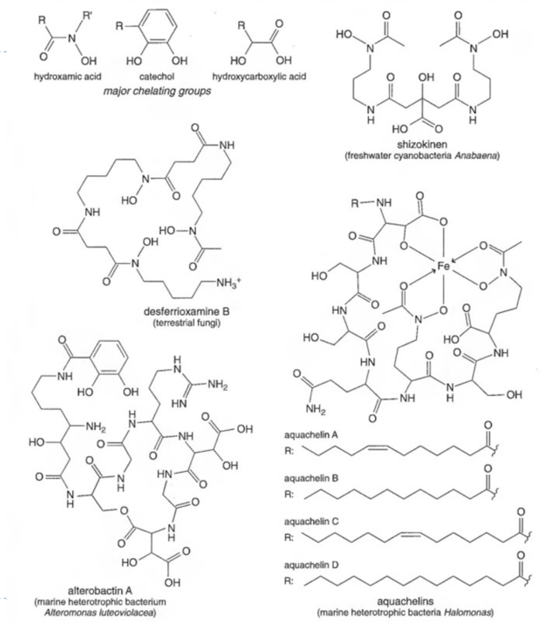

Fig. 3.11 Major iron(III)-chelating groups in siderophores and structures of some siderophores.

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Van Krevlin Plot

Table 4.5 Coal analysis (ASTM procedures; after Ward 1984)

proximate analyses	
moisture	drying at 110 °C (avoiding oxidation and decomposition)
volatile matter	volatiles liberated at 950 °C in absence of air, excluding moisture
ash	inorganic residue from combustion
fixed carbon	C remaining after volatiles determination (i.e. coking potential)
ultimate analyses	
elemental analysis	C, H, N and S content
oxygen	determined by difference (i.e. total minus C, H, N, S content, and correcting for inorganic mineral content); more rarely determined directly
examples of other analyses	
forms of sulphur	organic, sulphide, native S, sulphate
other elements	e.g. trace elements, phosphorus, chlorine, carbonate CO_2
relative density	depends on ash content and maturity
specific energy	energy liberated upon combustion

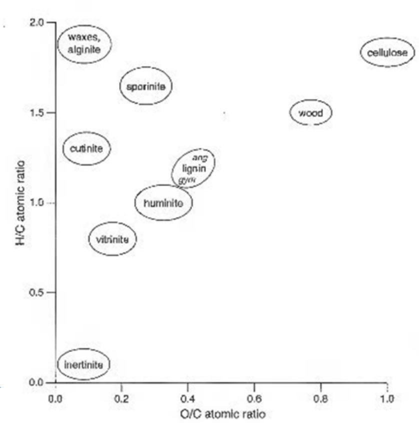

Fig. 4.3 Chemical composition of major coal macerals and plant tissues plotted on a van Krevelen diagram (after Tissot & Welte 1984; Hedges et al. 1985). Lignin incorporates differences between angiosperms (*ang*) and gymnosperms (*gym*) (after Hatcher 1990).

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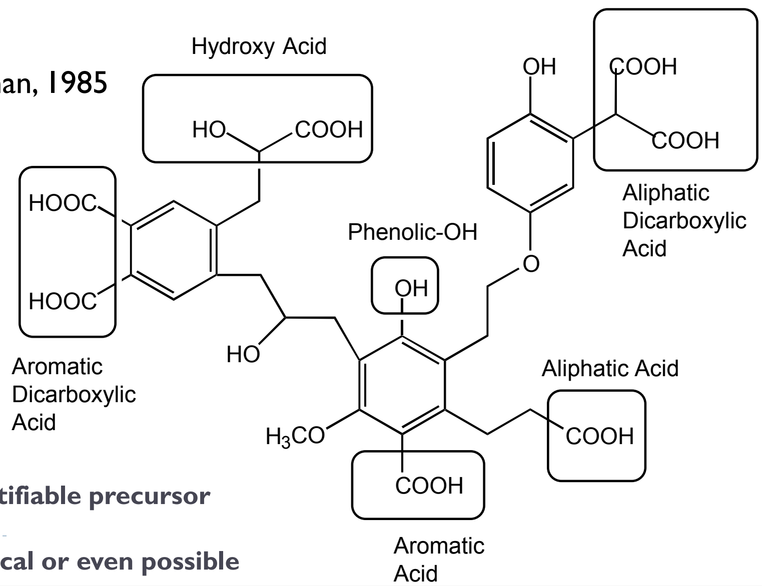
Putting it all together?

From Thurman, 1985



- **Many identifiable precursor structures**
- **Not practical or even possible**

Concentrations: Pedogenic

- Land Sources
  - From Woody & non-woody plants, lignin, etc.
  - Depends on vegetation, soil, hydrology
- Attenuated by adsorption to clay soils
  - Parallel watersheds in Australia (Cotsaris et al., 1994 [Chamonix proceedings])
    - Clearwater Creek, high clay content: 2.5 mg/L TOC
    - Redwater Creek, sandy soil: 31.7 mg/L TOC

Concentrations: Aquagenic

- Algal & aquatic plant Sources
  - Depend on nutrient levels / trophic state
- Concentrations in Lakes (mg/L) (Thurman, 1985)

Trophic State	Mean DOC	Range
Oligotrophic	2	1-3
Mesotrophic	3	2-4
Eutrophic	10	3-34
Dystrophic	30	20-50

- Groundw
  - No algae

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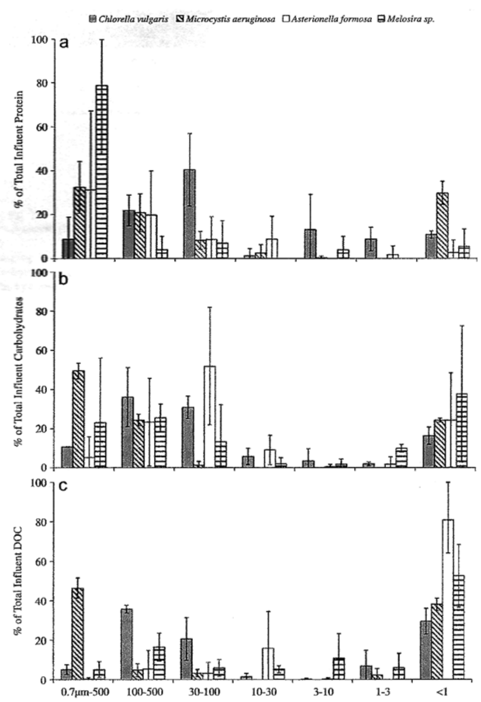
MW vs type

- Algogenic organic matter (AOM)
  - Proteins & carbohydrates
  - Large polymers with monomers



Henderson et al., 2008

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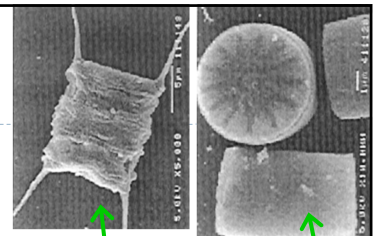
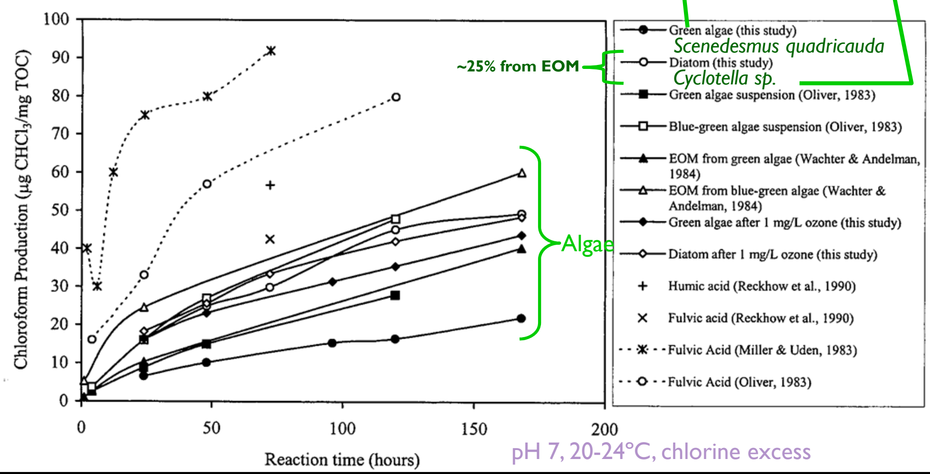
Algae as THM Precursors

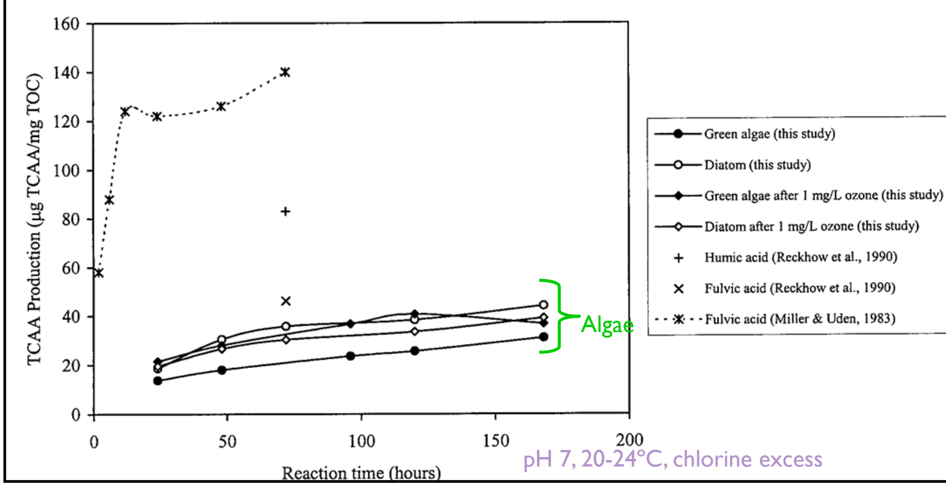
- From: Plummer & Edzwald, 2001
  - [ES&T:35:3661]





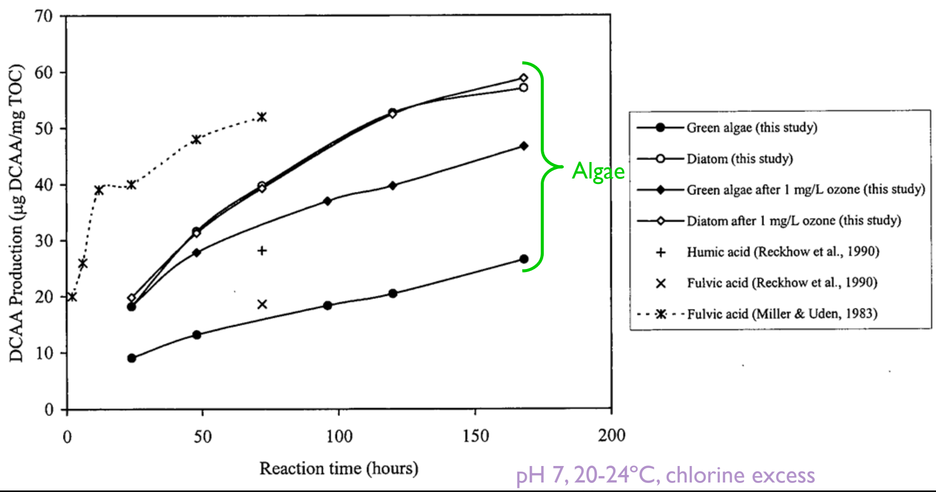
Algae as TCAA Precursors

- Not much impact?



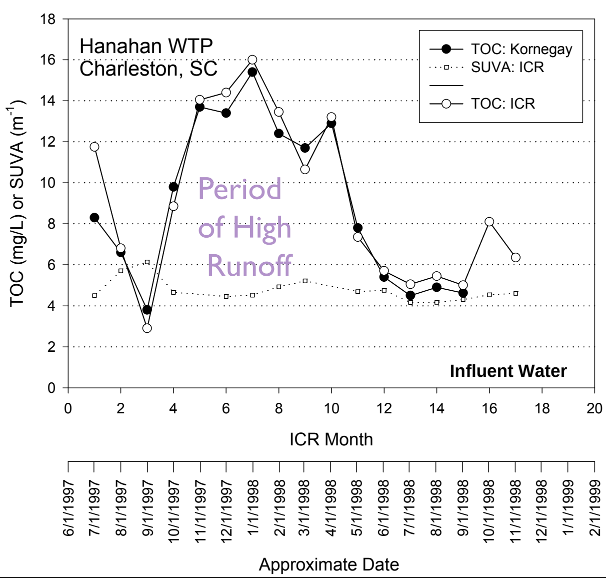
Algae as DCAA Precursors

- Are Algae important sources of dihalo-AA precursors?



Annual TOC Cycles

- Edisto River
  - Former source for Charleston's (SC) Hanahan WTP
  - Flushing of TOC during high rainfall months (cold period)



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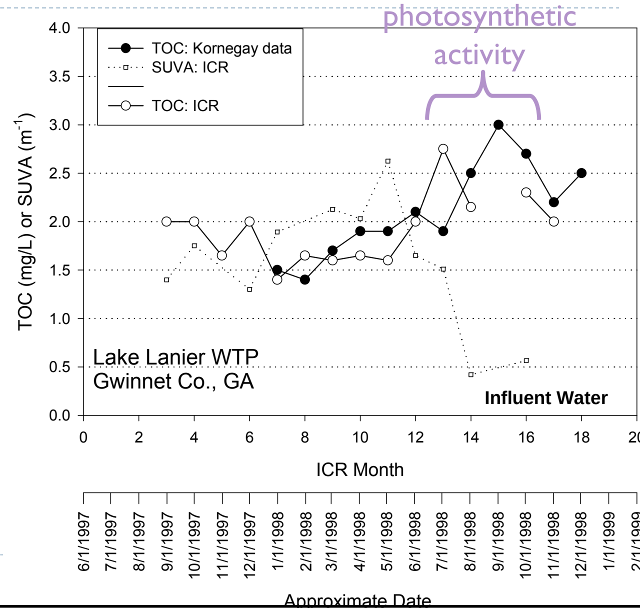
Annual TOC Cycles

- Lake Lanier
  - Source for Gwinnett Co.'s (GA) Lanier WTP
  - High clay content in watershed



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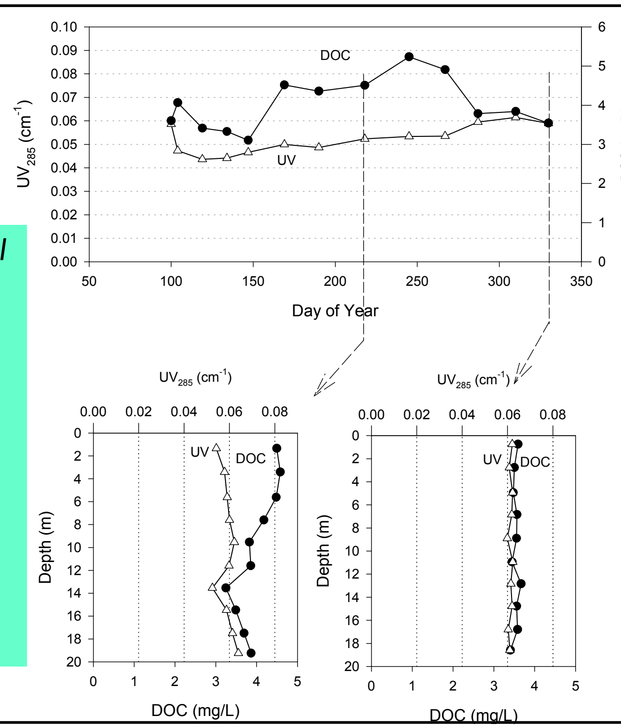

Spatial and Temporal Distribution of DOC and UV absorbing Substances in Lake Bret

(from Zumstein & Buffle, 1989; and Krasner et al., 1996)

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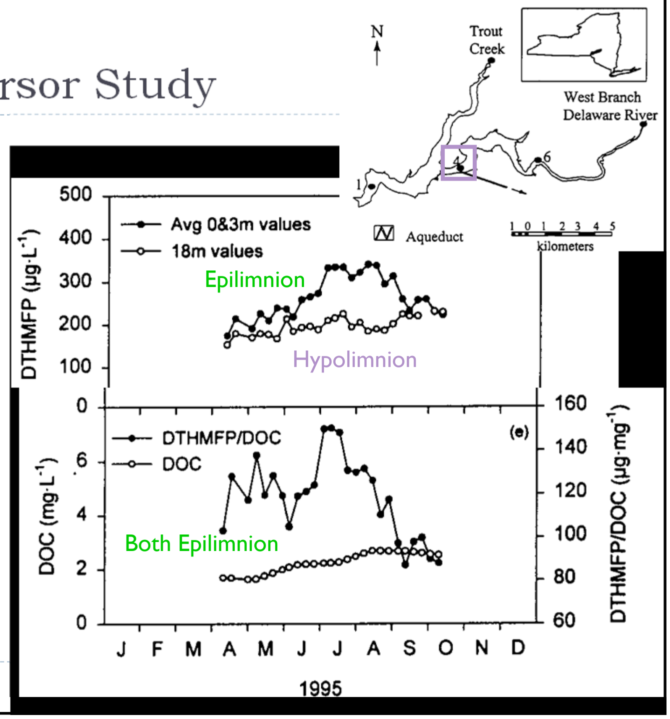
THM Precursor Study

- Cannonsville Reservoir
  - Catskill-Delaware water supply for NYC
- Stepczuk et al., 1998
  - J. Lake Res. Mgmt. 14(2-3)356



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Biochemicals

Metabolic

Formation Potential

Sugars, starches	Low
Proteins	Moderate
Cellulose	Low
Hemicellulose	Low
Fats & waxes	Low
Lignins & phenolics	high

Decreasing biodegradability

Structural

Terpenoids - ??

- Simplification: Doesn't explicitly consider bacterial metabolites

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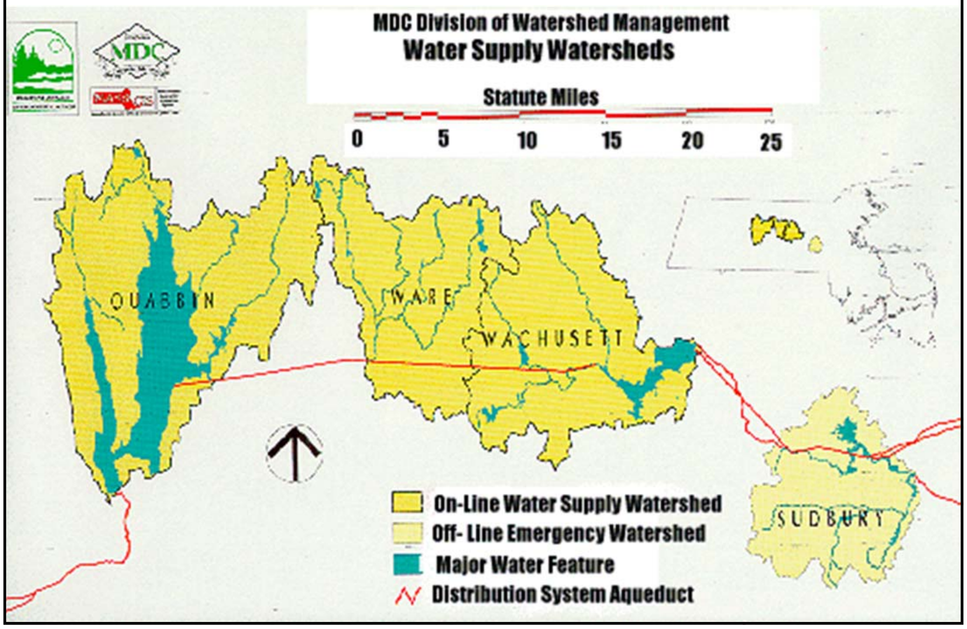
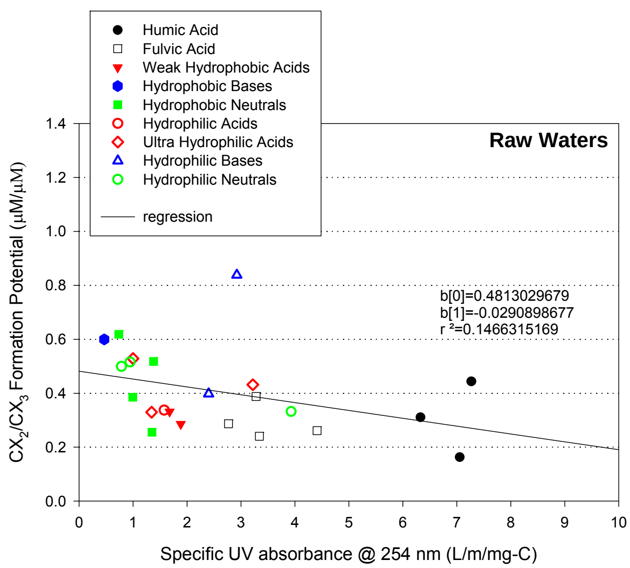


Dihalo and Trihalo DBPs

- NOM Fractions
  - Evidence for greater importance of dihalo species in non-lignin based NOM



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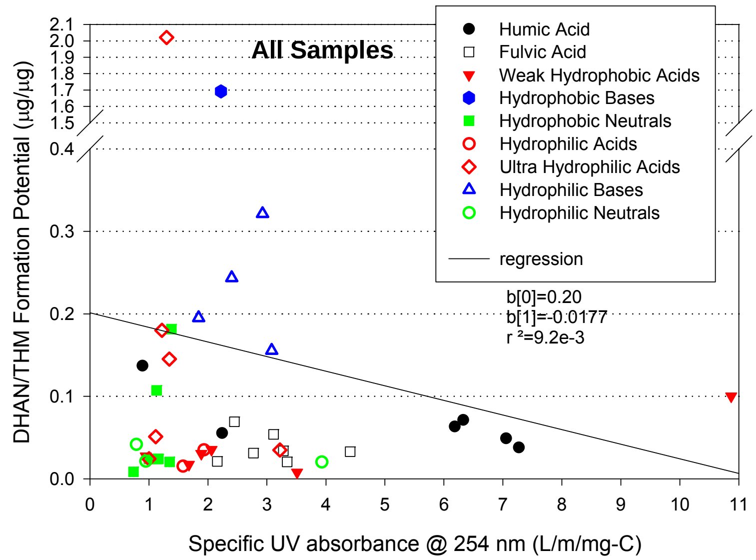
DHAN/THM Ratio vs SUVA



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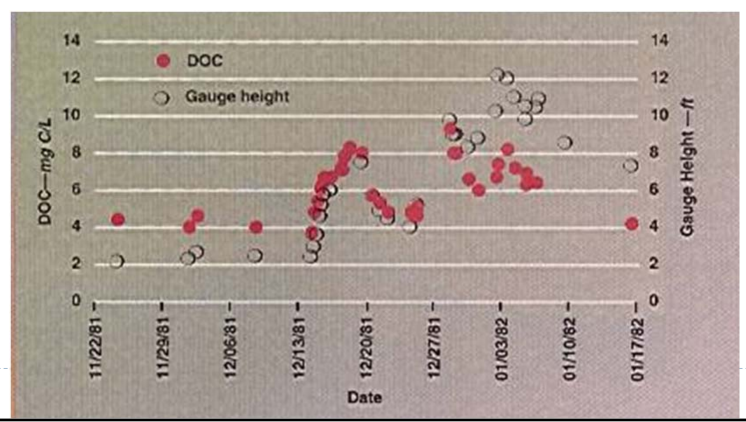
DOC and runoff

- Ogeechee River (GA)
  - From Aiken & Cotsaris, 1995
    - [JAWWA 87(1)36]



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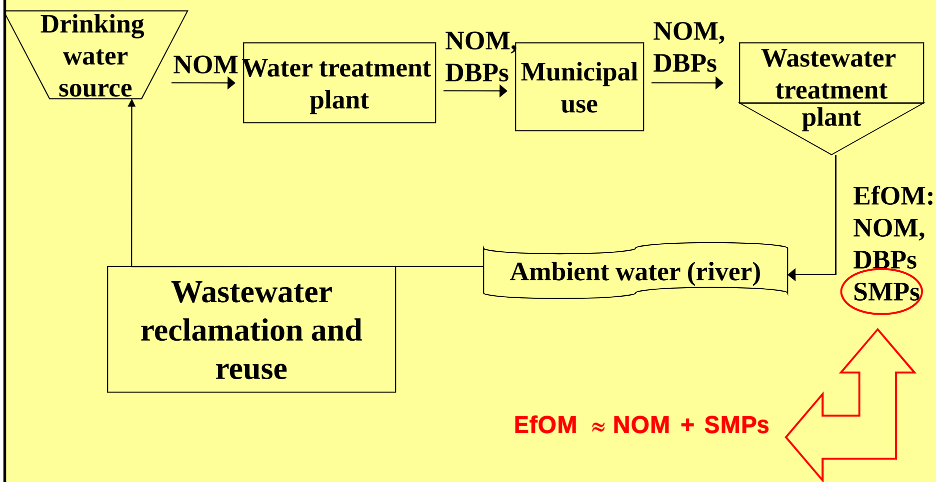
What is EfOM?



from: Krasner & Amy

- To next lecture