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CEE 697z
Organic Compounds in Water and Wastewater

Origins of NOM I

Lecture #4

Outline

- Engineering Concerns
- NOM in Source Waters
  - Origins
  - Classifications
  - Concentrations
- Characterization of NOM
  - Basic properties
  - Useful methods
- Reactions with Disinfectants
  - Compounds formed
  - Amounts formed: Precursor tests

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

Source of NOM

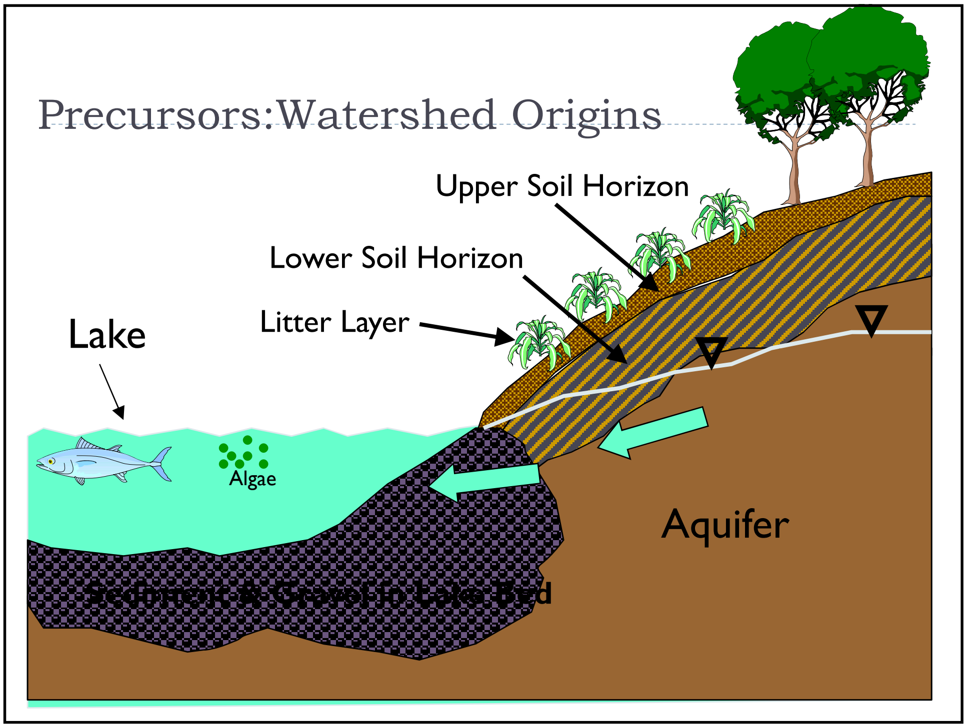
- Where
  - Pedogenic
  - Aquogenic
- Factors
  - Geology
  - Flora
  - Climate
  - Land use
  - Hydrology

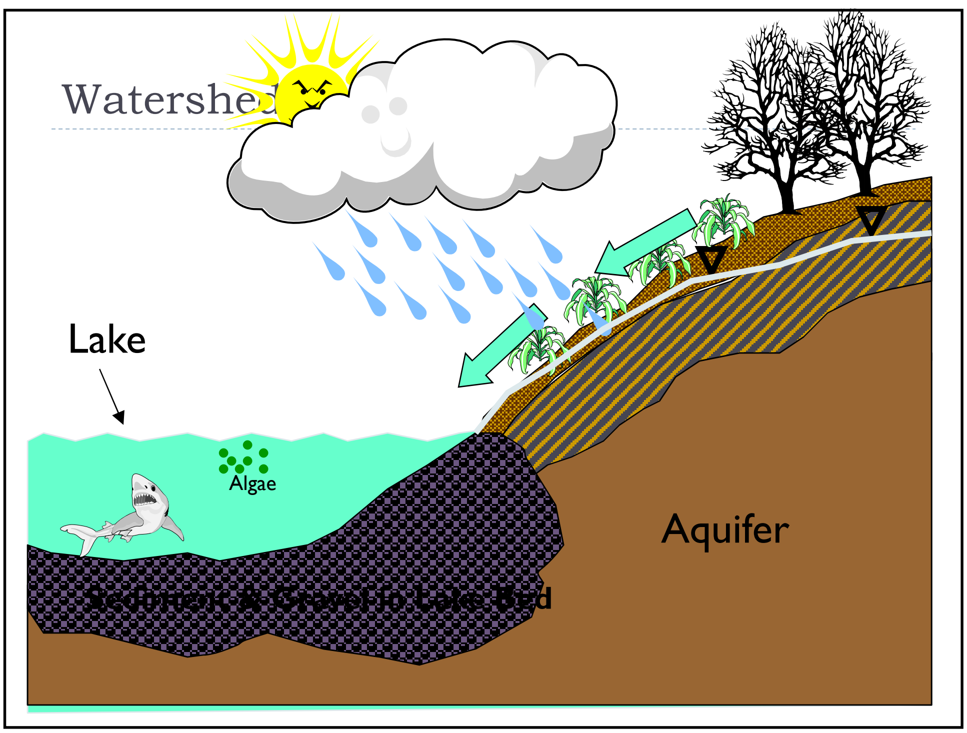
Some definitions

Groupings Based on Origin

- **autochthonous** material is formed within the water body
- **allochthonous** material can originate from either the soil or from upstream water bodies

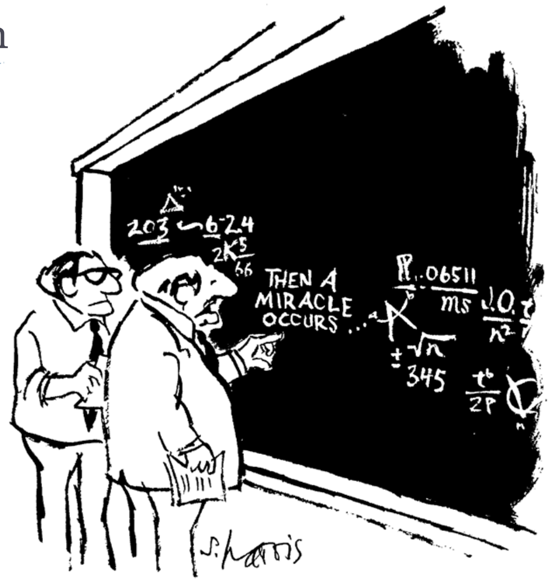
- aquagenic, substances originating from any water body
- pedogenic for substances originating from soil


Precursors:Watershed Origins
Upper Soil Horizon
Lower Soil Horizon
Litter Layer
Lake
Algae
Aquifer
Sediment & Gravel in Lake Bed


Watershe
Lake
Algae
Aquifer
Sediment & Gravel in Lake Bed

DOC Generation

- What do we know?
- Start with the "building blocks"
- Link to chemical characterization



"I think you should be more explicit here in step two"

The terminology

- Humic substances
  - Fulvic & Humic Acid
- Non-humics
  - Many are Structurally Defined
  - Many are simple plant products
    - Tannins, Aromatic Acids and Phenols
    - Carbohydrates, sugars
    - Fatty Acids
    - Amino Acids and Proteins
    - Terpenoids
    - Miscellaneous Low MW Compounds
  - Acylheteropolysaccharides are in this group too
    - Structural sugars containing nitrogen

NOM: Origins & Behavior

- Humic substances (humic and fulvic acids)
  - Organic detritus modified by microbial degradation
  - lignin origin vs microbial
  - resistant to further biodegradation
  - "old" organics
  - easier to remove by coagulation
- Non-humics & Structurally-defined groups
  - may be relatively "new"
  - includes many biochemicals and their immediate degradation products
  - generally more biodegradable
  - concentrations are highly variable with season

Origins

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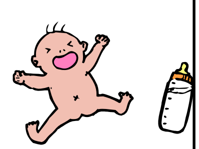
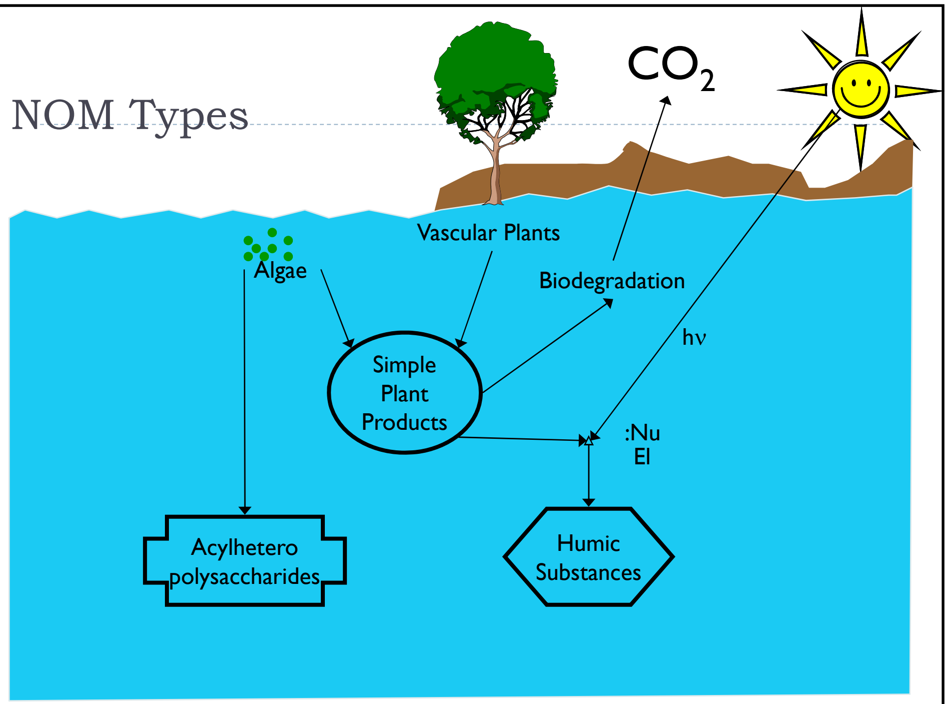
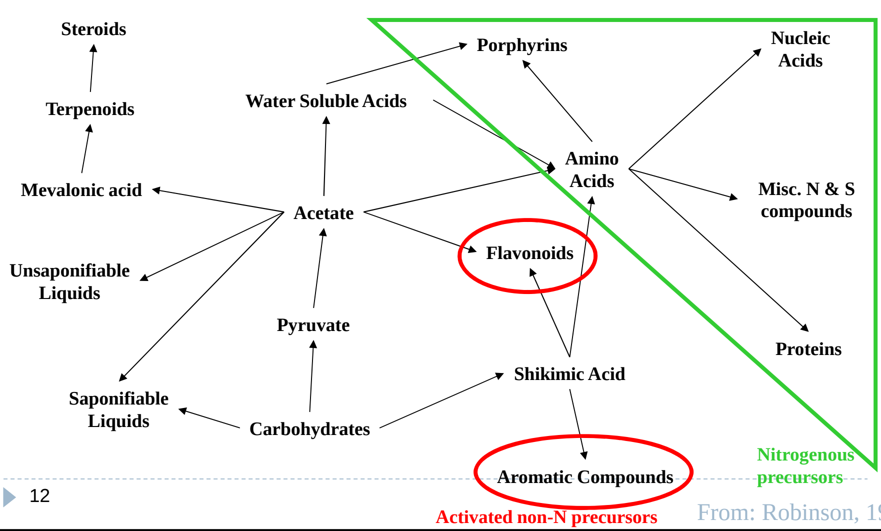


NOM Types



Simple Plant Products: Metabolic Pathways



From: Robinson, 1991

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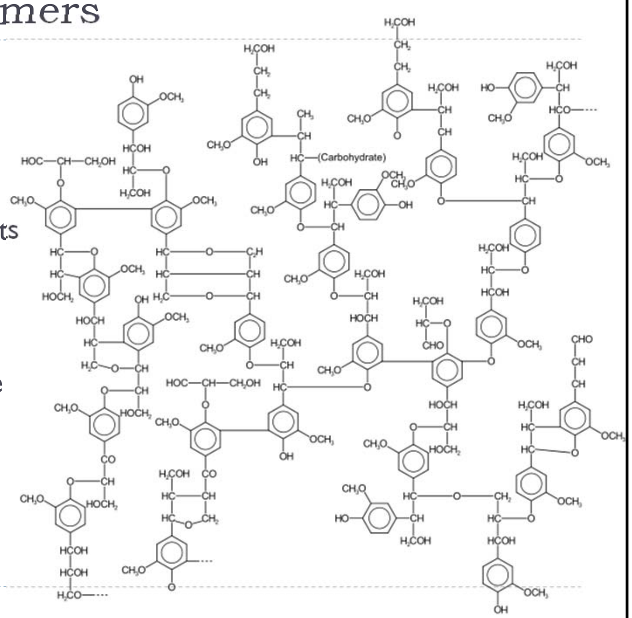
Aged leaves from 3 locations in Wachusett watershed

Leaching Experiments

White Pine | White Oak | Red Maple

Plant biopolymers

- Cellulose
- Lignin
  - Phenyl-propane units
  - Cross-linked
  - Radical polymerization
  - Ill defined structure
- Hemicellulose
- Terpeniods
- Proteins



Leaching Rates

- Leaching rates from the scientific literature
- Amount released each week
  - Diminishes with time for some, accelerates for others

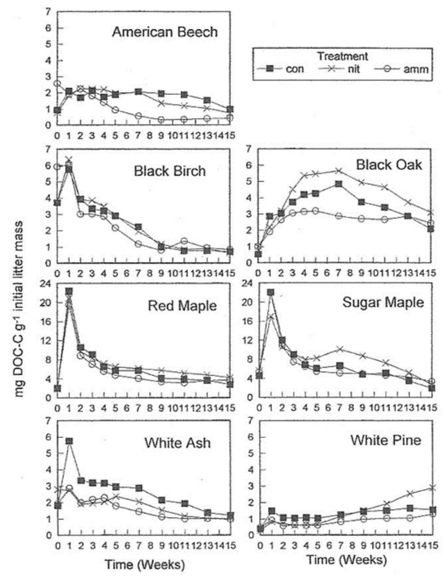


Fig. 2. Time series graphs of weekly DOC-C leached from decomposing litter over the 15 weeks as mg C g^{-1} initial litter. Each point represents the mean of four replicate cups within each species and treatment. Note the scale differences for red and sugar maple litter. Statistical data presented in Table 3.

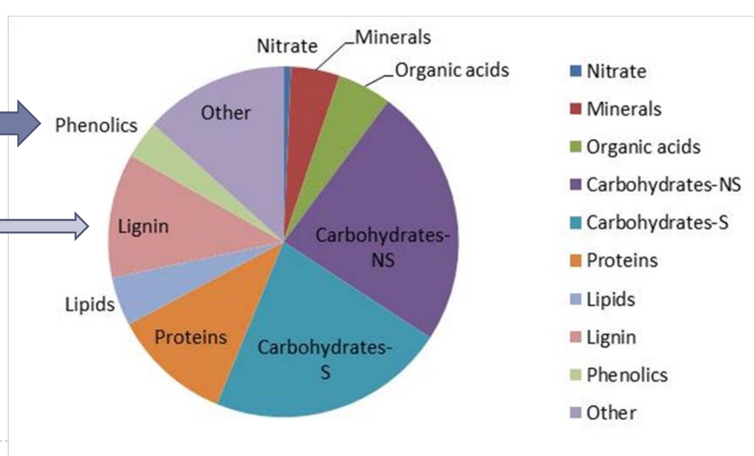
From: Magill and Aber, 2000
Soil Biology & Biochemistry, vol. 32, pp.603-613

Composition of an "average" leaf

- 250 g/m^2/yr EABP

Highly-colored

Some color



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Variations based on Species

TABLE 12.1 Concentration of Major Carbon Compunds in Different Plant Materials
(Data from McClaugherty et al. 1985, Larsson and Steen 1988, Morrison 1980, Hodson et al. 1984)

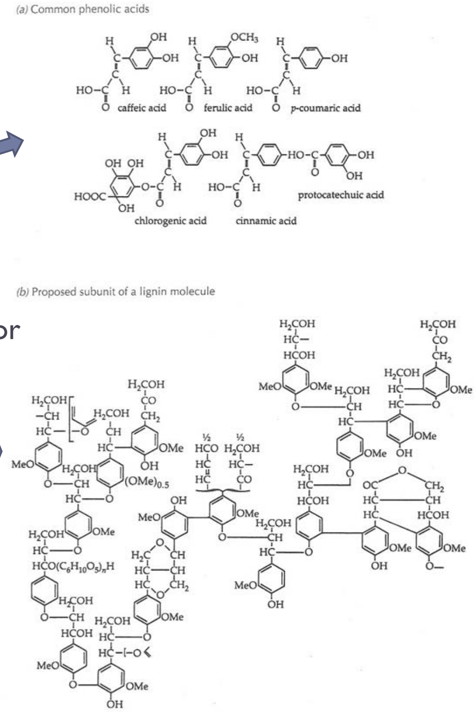
	Sugars and Starch (%)	Other Solubles (%)	Cellulose (%)	Lignin (%)
Woody plants				
Foliage				
Sugar maple	7.2	37.6	43.1	12.1
Red oak	7.3	25.1	47.4	20.2
White pine	5.7	27.1	44.7	22.5
Fine roots				(Suberin)
Sugar maple	3.9	14.6	47.7	33.8
White pine	5.2	20.0	49.5	25.3
Wood				
Red maple	1.1	5.9	80.5	12.5
Hemlock bark	4.1	16.7	40.3	38.9
Herbaceous plants				
Foliage and stems				
Salt marsh grass				
Tall-form, live		34.4	52.5	13.1
Tall-form, dead		28.9	57.7	14.4
Tall-form, stems		30.3	56.0	13.7
Ryegrass stems				3–9
Leaves				2–6
Timothy stems				5–9
Leaves				3–6
Roots				
Salt marsh grass		36.2	41.6	12.2
Mixed pasture grasses		20	58	22

- Source:
  - Terrestrial Ecosystems
    - Aber & Melillo
    - 2nd edition
    - Harcourt Academic Press

Colored Compounds

- Phenolic Acids
  - Readily released, highly colored
- Lignin
  - Very slowly released, some color

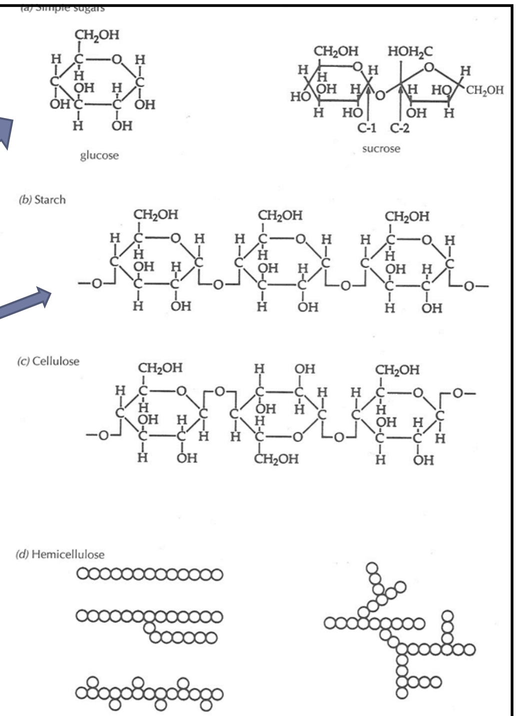
(a) Common phenolic acids



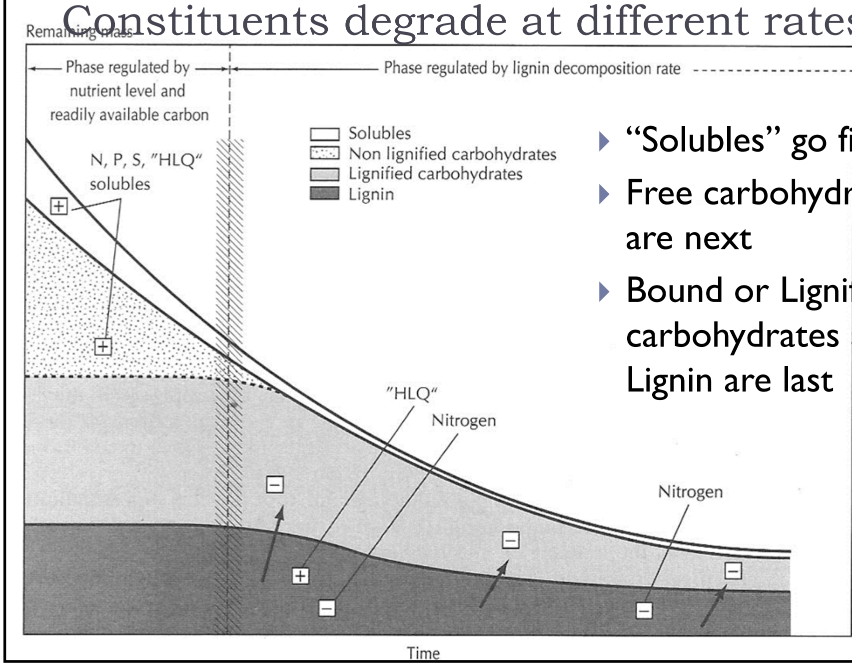
(b) Proposed subunit of a lignin molecule

Colorless Compounds

- Simple sugars
  - Readily released, highly biodegradable
- Starch
  - Easily released and also biodegradable
- Cellulose & Hemicellulose
  - Slow to solubilize, not … degraded



Constituents degrade at different rates



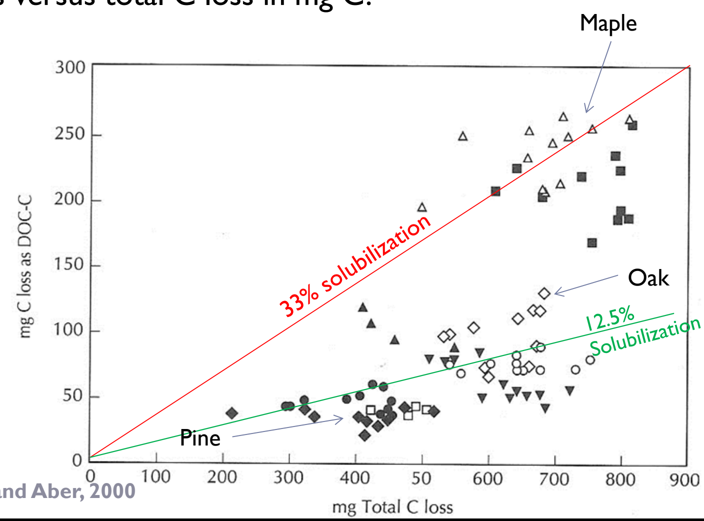
- "Solubles" go first
- Free carbohydrates are next
- Bound or Lignified carbohydrates and Lignin are last

Solubilization vs Total Loss

- DOC-C loss versus total C loss in mg C.

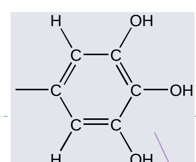
Y-axis values are mean leached DOC concentration for the 15 week treatment

X-axis values are total C loss from litter.



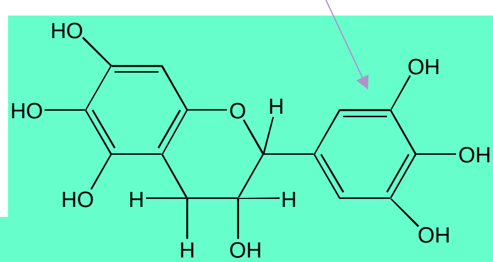
Re-drawn from Magill and Aber, 2000

Tannins, Aromatic Acids and Phenols



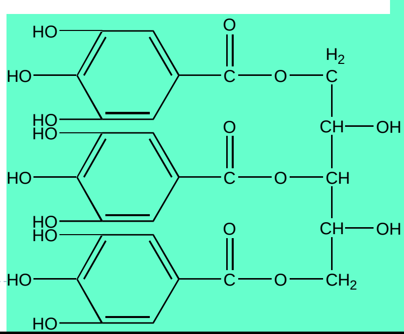
Chemical Symbols

- About 0.5% of Total
- Plant Products
- Likely THM Precursors
- Source of Color & DBPs



Condensed Tannin

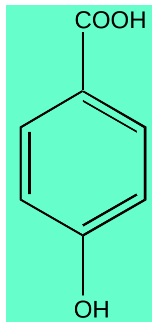
Gallic Acid monomers



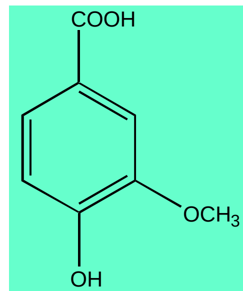
Hydrolyzable Tannin

Tannins, Aromatic Acids and Phenols, cont.

- Lignin monomers

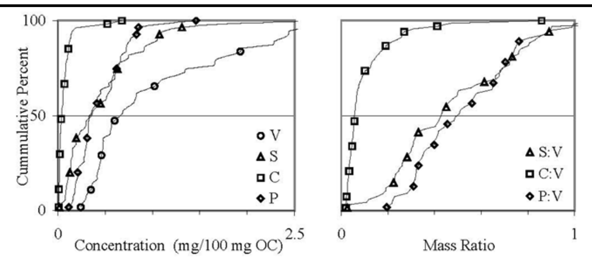


p-Hydroxybenzoic Acid



Vanillic Acid

Lignin



Lignin Phenol Group	Obs.	Concentration (mg/100 mg OC) Range	Median	Mean	Std. Dev.
Vanillyl[a] (V)	57	0.24 - 3.18	0.68	1.02	0.78
Syringyl[b] (S)	55	0.02 - 2.88	0.36	0.50	0.50
Cinnamyl[c] (C)	54	0.01 - 0.68	0.04	0.07	0.11
p-Hydroxy[d] (P)	57	0.12 - 1.46	0.36	0.45	0.27
Total Lignin Phenol[e]	55	0.59 - 6.66	1.41	2.06	1.47

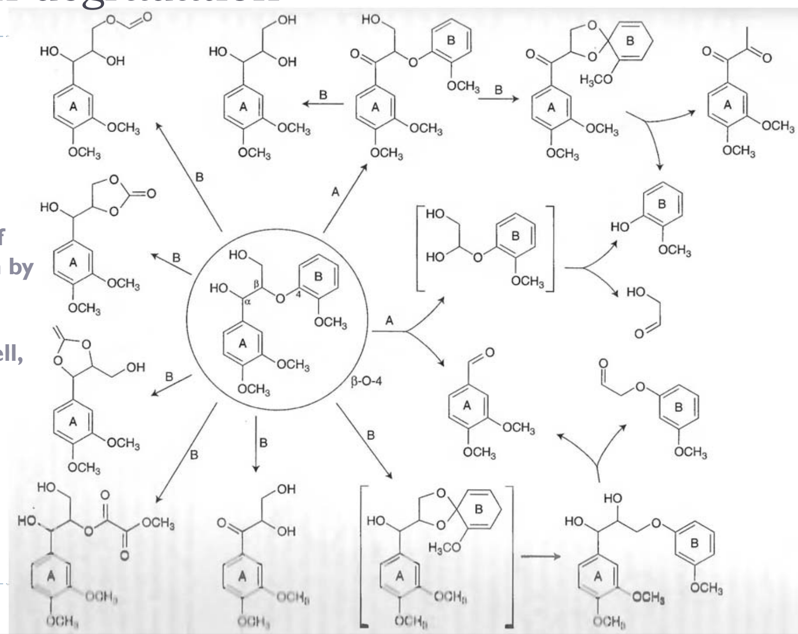
	Obs.	Mass Ratio (Relative to Vanillyl Content) Range	Median	Mean	Std. Dev.
Syringyl (S:V)	68	0.03 - 1.75	0.43	0.50	0.32
Cinnamyl (C:V)	68	0.02 - 0.86	0.06	0.11	0.13
p-Hydroxy (P:V)	55	0.19 - 1.22	0.51	0.54	0.23

	Obs.	Concentration Range	Median	Mean	Std. Dev.
Total Lignin[e] ($\mu g\ L^{-1}$)	55	0.42 - 39.4	9.7	10.7	9.8
% DOC as Lignin	55	0.24 - 3.12	0.6	1.0	0.7

From:
Perdue & Ritchie, 2004

Lignin degradation

Oxidation of model lignin by ligninase & H_2O_2 (from Kirk & Farrell, 1987)



- [To next lecture]