Source, Composition and Reactivity of DOM in Estuaries

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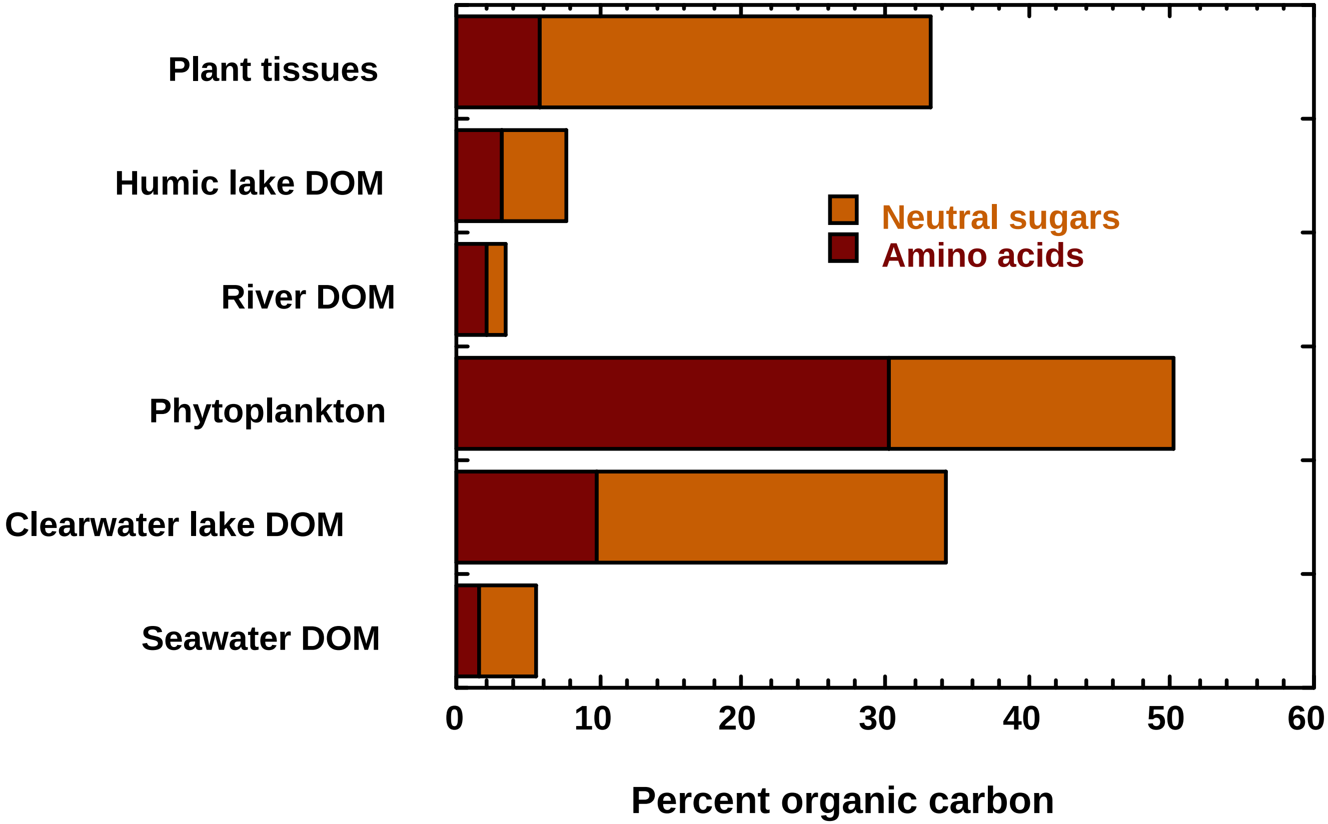
- DOM is more dynamic than indicated by bulk measurements
- Multiple sources of DOM exist with different compositions and reactivities
- DOM removal processes are chemically selective
- Molecular analyses indicate DOM sources, transformations and bioavailabilty

10th International Estuarine Biogeochemistry Symposium
Xiamen University, May 18-22, 2008

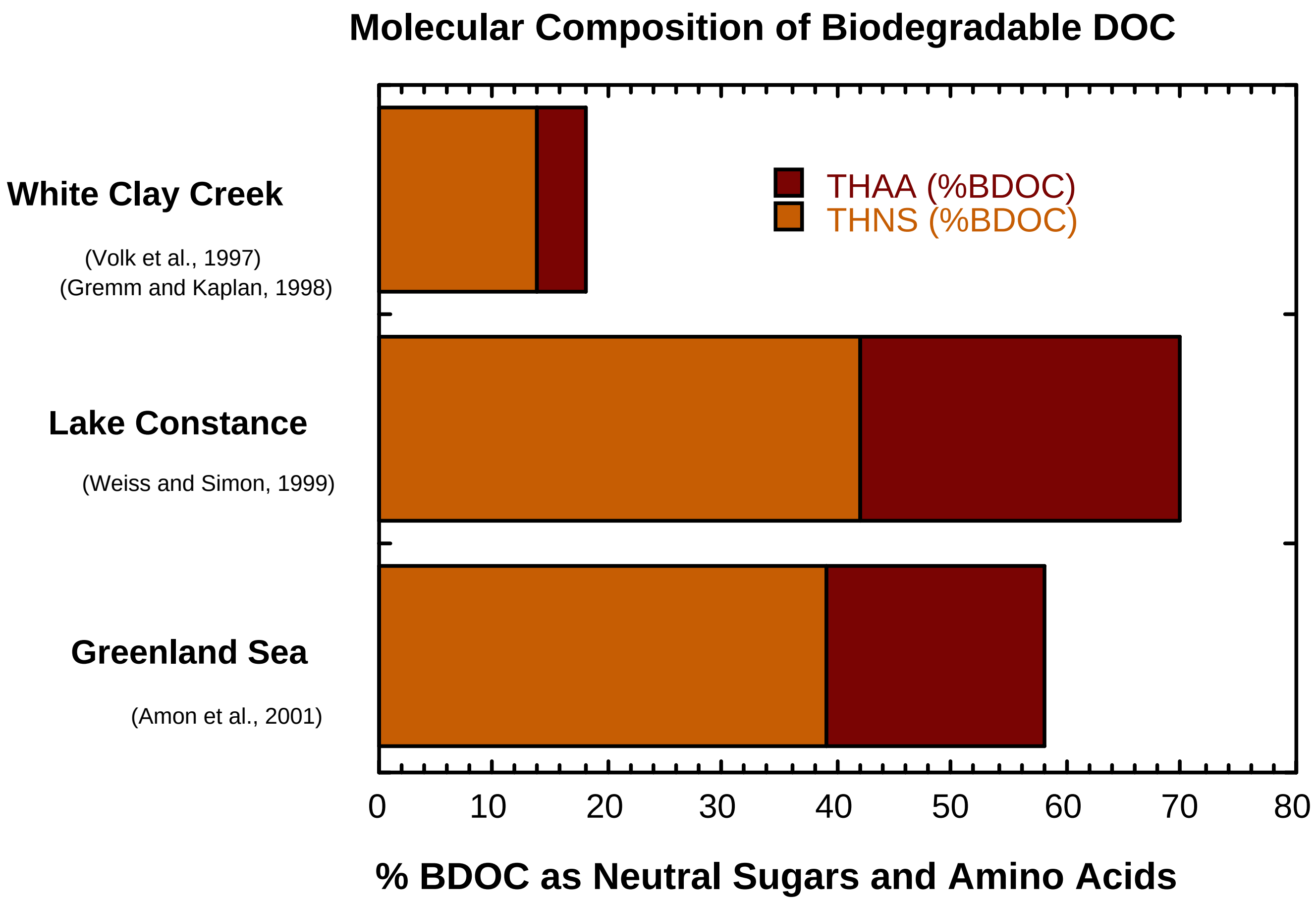
Combined amino acids and neutral sugars are abundant biomolecules

- they are major components of vascular plants and phytoplankton
- they are found in lake, river and seawater DOM



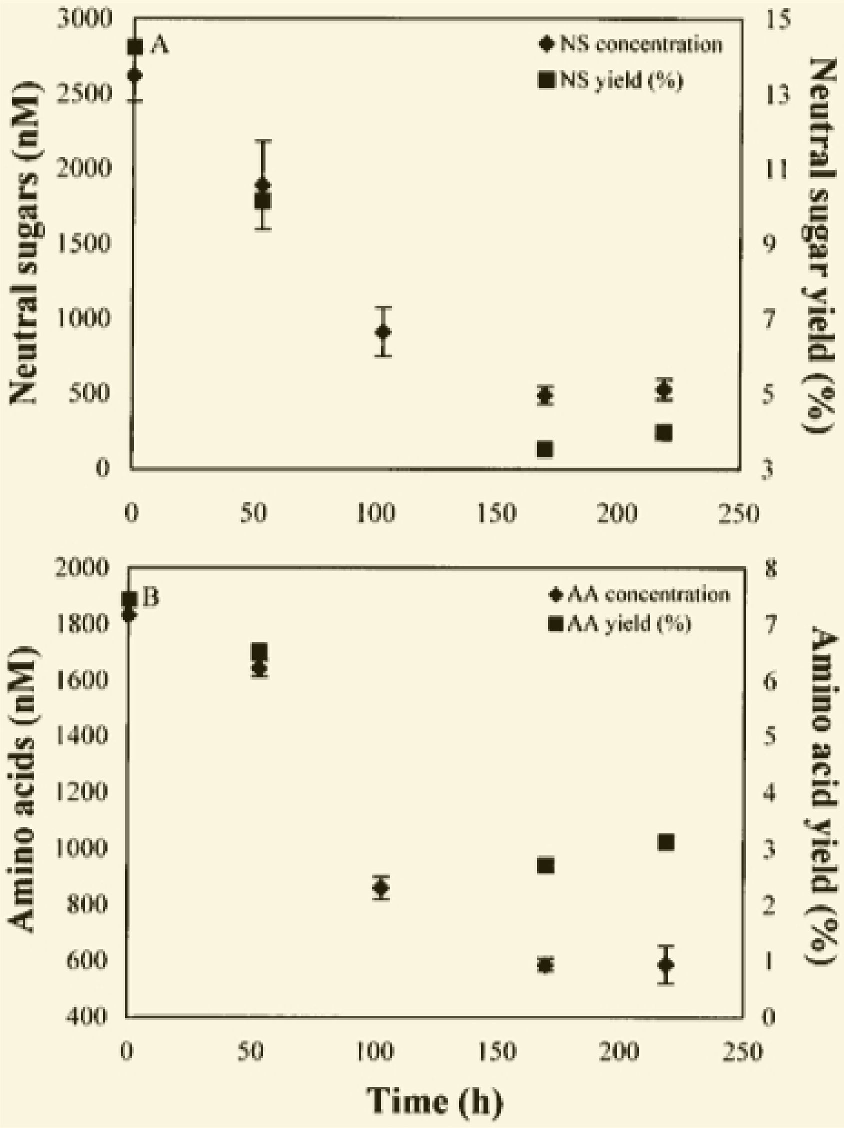
Combined amino acids and neutral sugars are very bioreactive

- they comprise a large percentage of biodegradable DOM



Biodegradation of diatom-derived DOM (Greenland Sea)

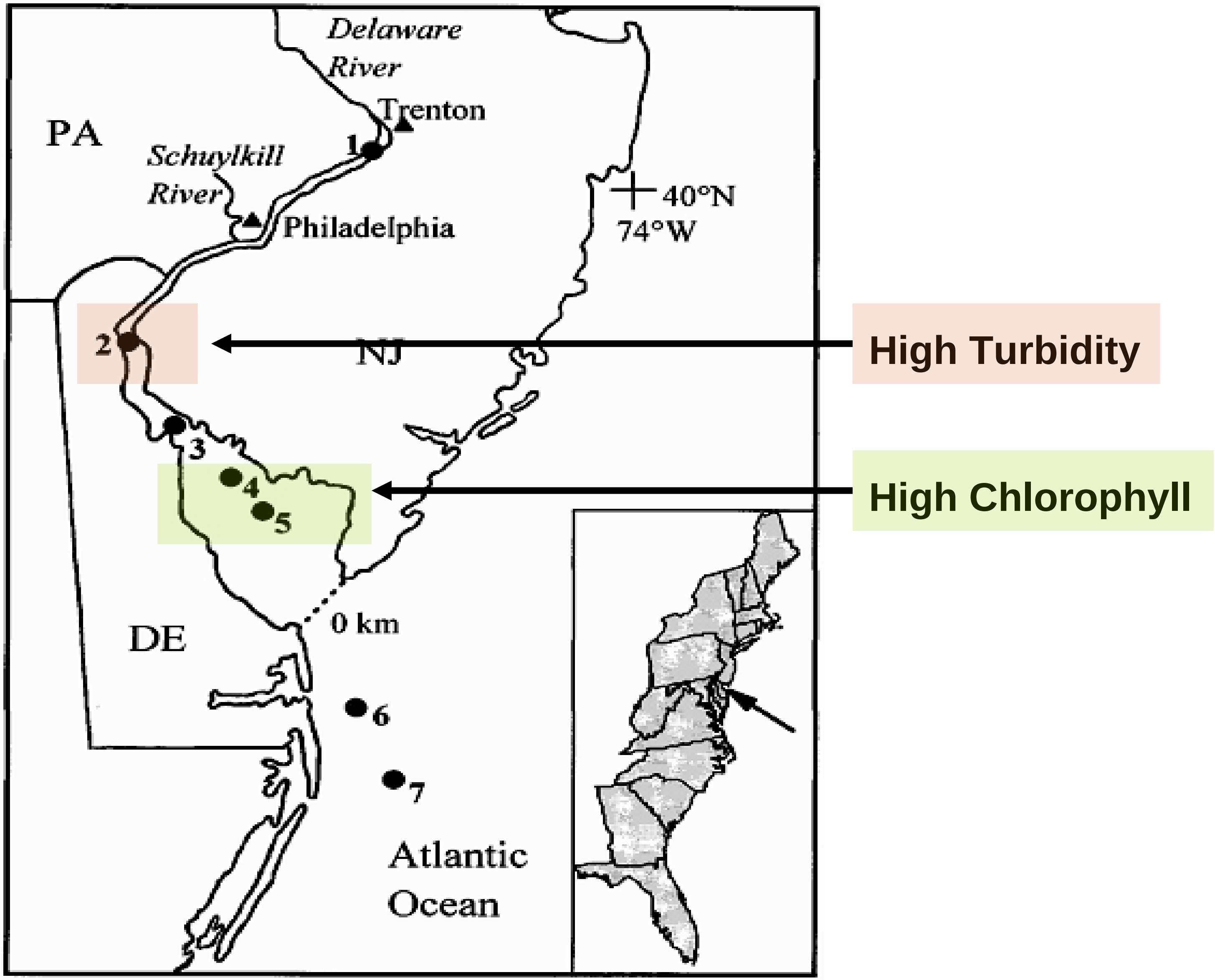
- dissolved combined neutral sugars and amino acids are preferentially utilized



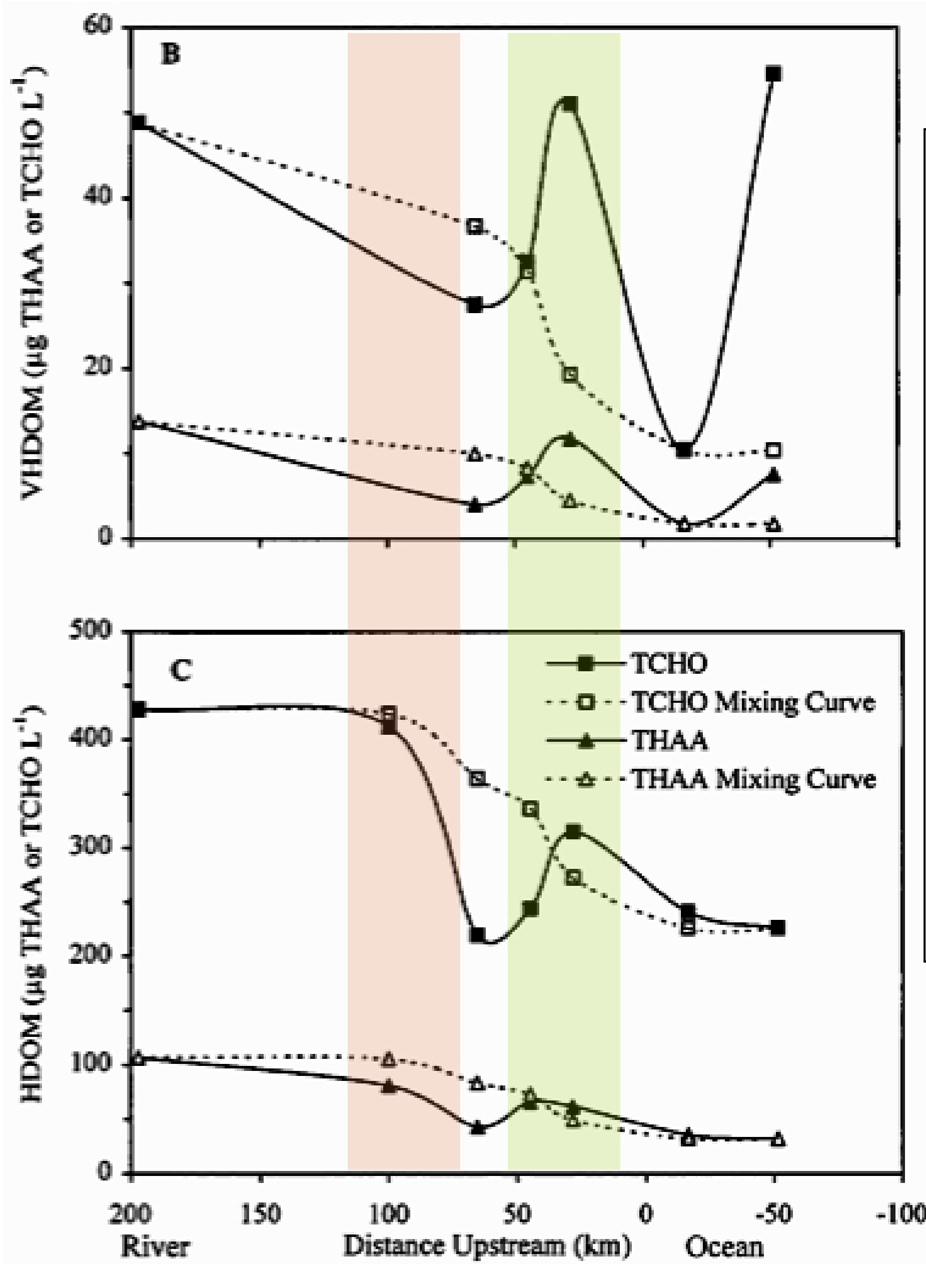
(Amon et al., 2001)

Dissolved combined amino acids and carbohydrates in Delaware Bay

(Mannino and Harvey, 2000. L&O 45: 775)



Dissolved combined amino acids and carbohydrates in Delaware Bay



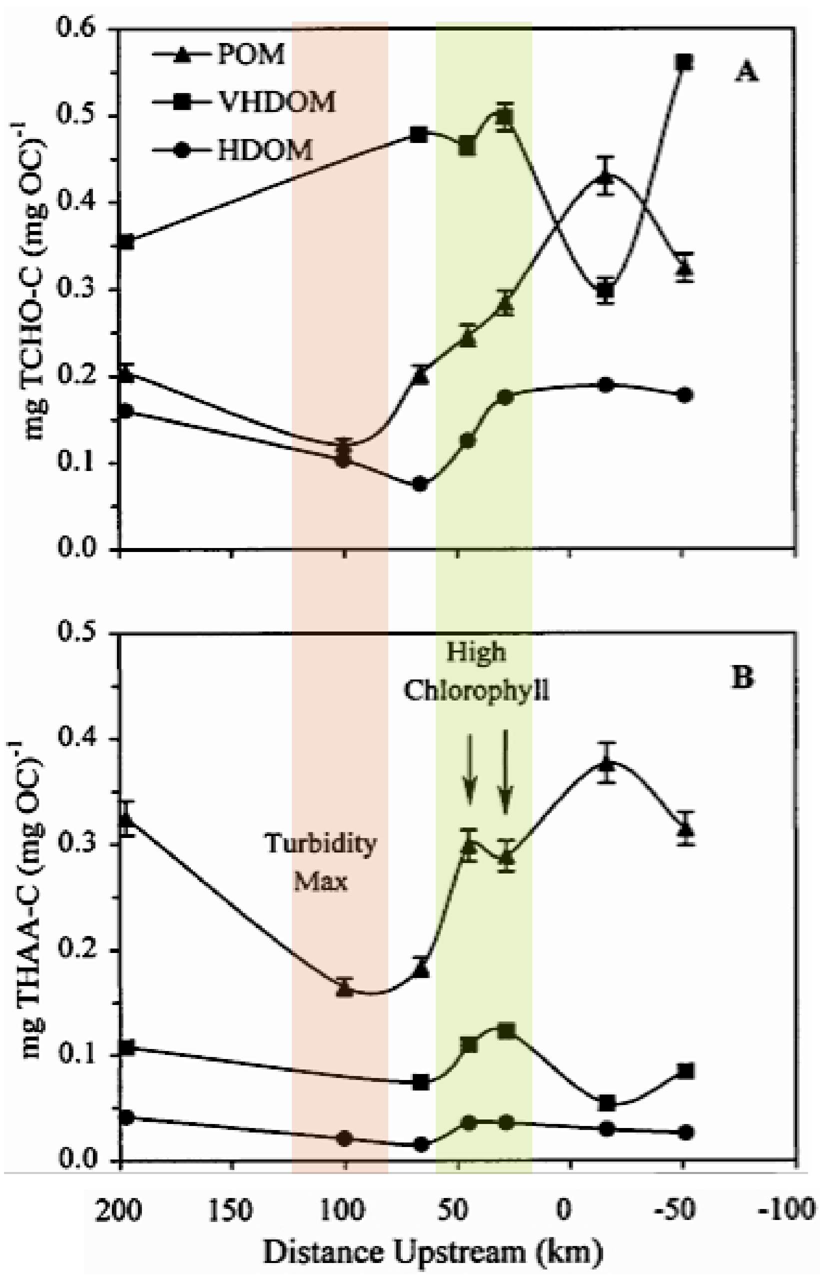
DOM isolated by ultrafiltration
(VHDOM = 30kDa - 0.2 µm)
(HDOM = 1 - 30kDa)

Mixing Curve - - - - -
indicates conservative mixing based on salinity

Sink of THAA and TCHO in high turbidity zone

Source of THAA and TCHO in high chlorophyll zone

Dissolved combined amino acids and carbohydrates in Delaware Bay



THAA and TCHO yields as a fraction of organic carbon

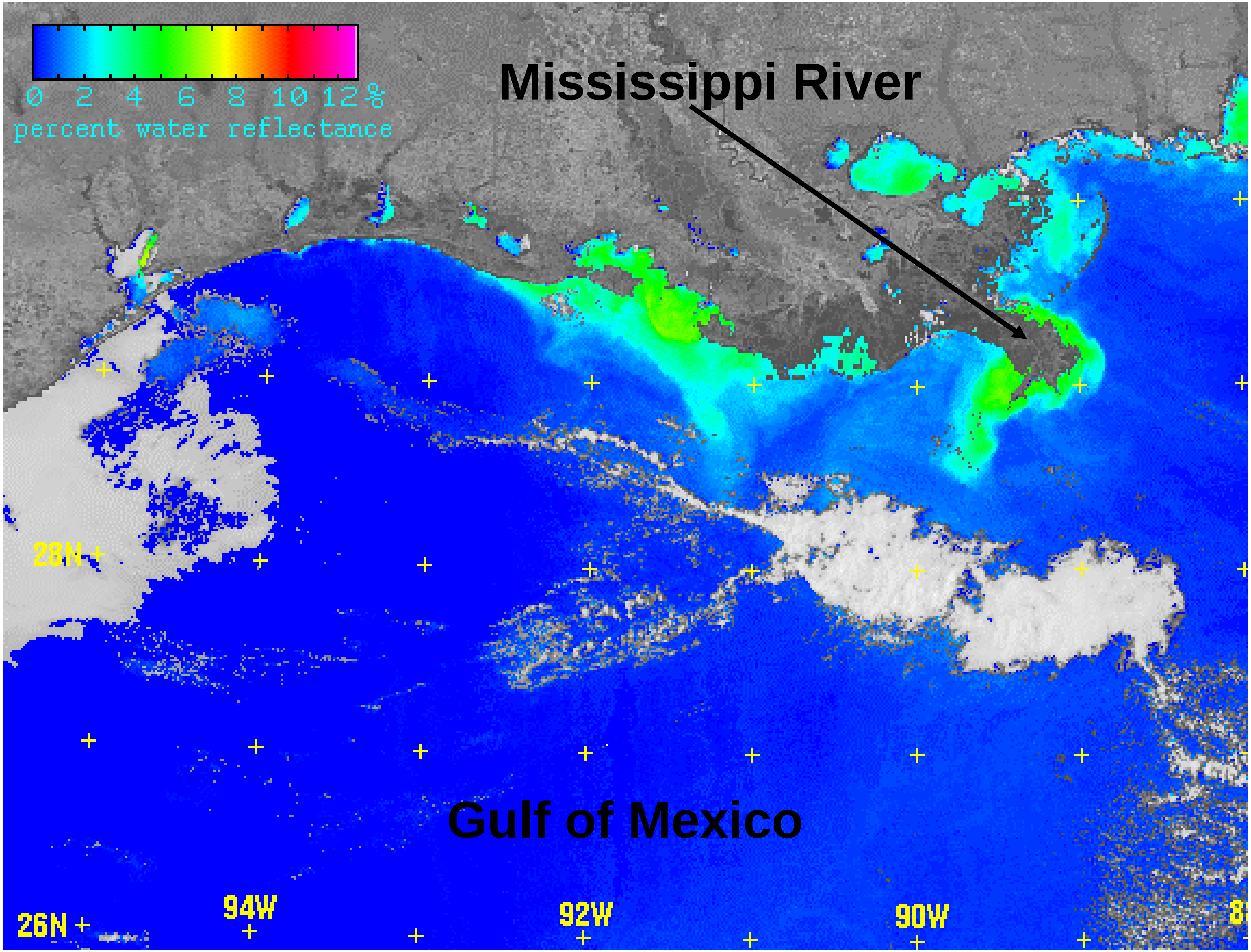
Yields increase in the high chlorophyll zone indicating a major input from plankton

Higher yields of THAA and TCHO indicate greater bioavailability of DOM

VHDOM is more bioavailable and less diagenetically altered than HDOM

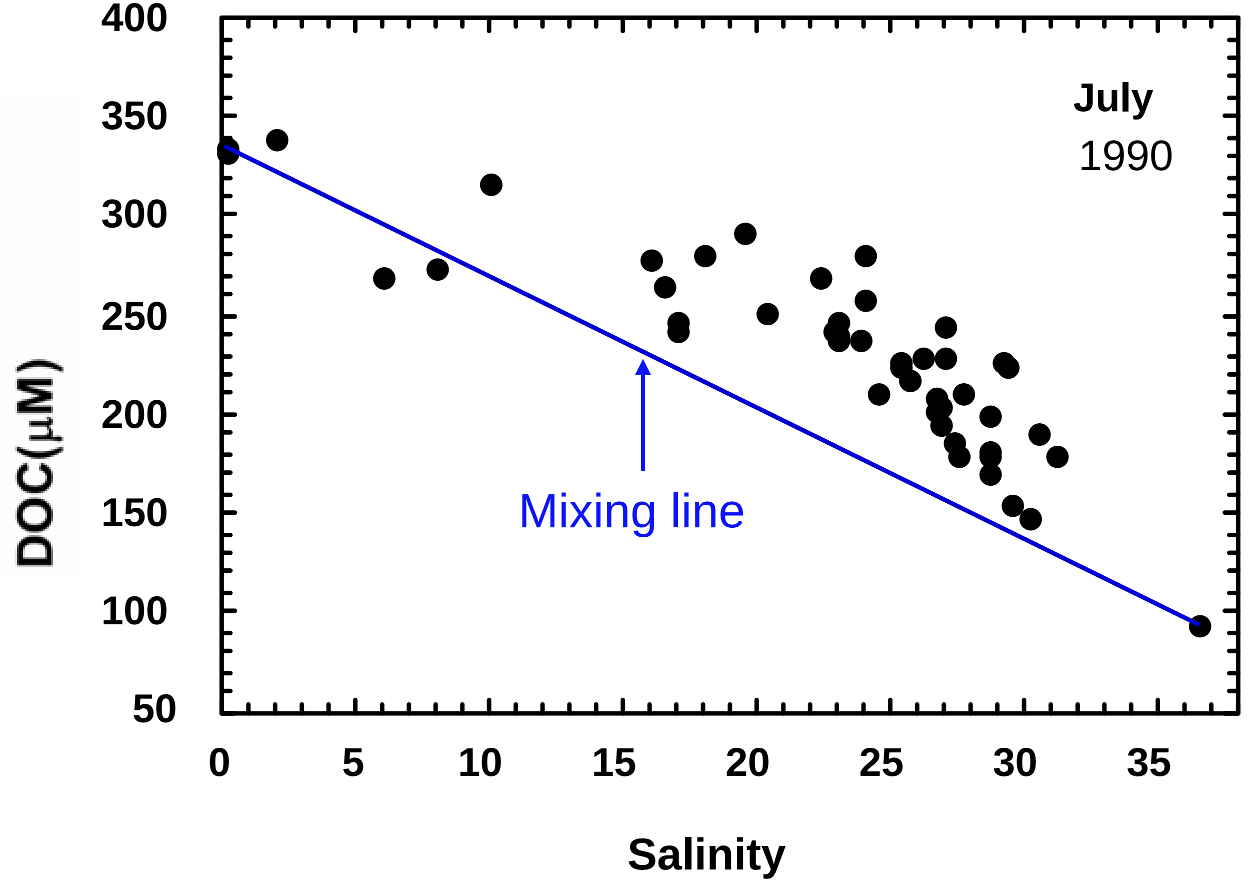
Size-Reactivity Continuum

DOM in the Mississippi River plume



DOM in the Mississippi River plume

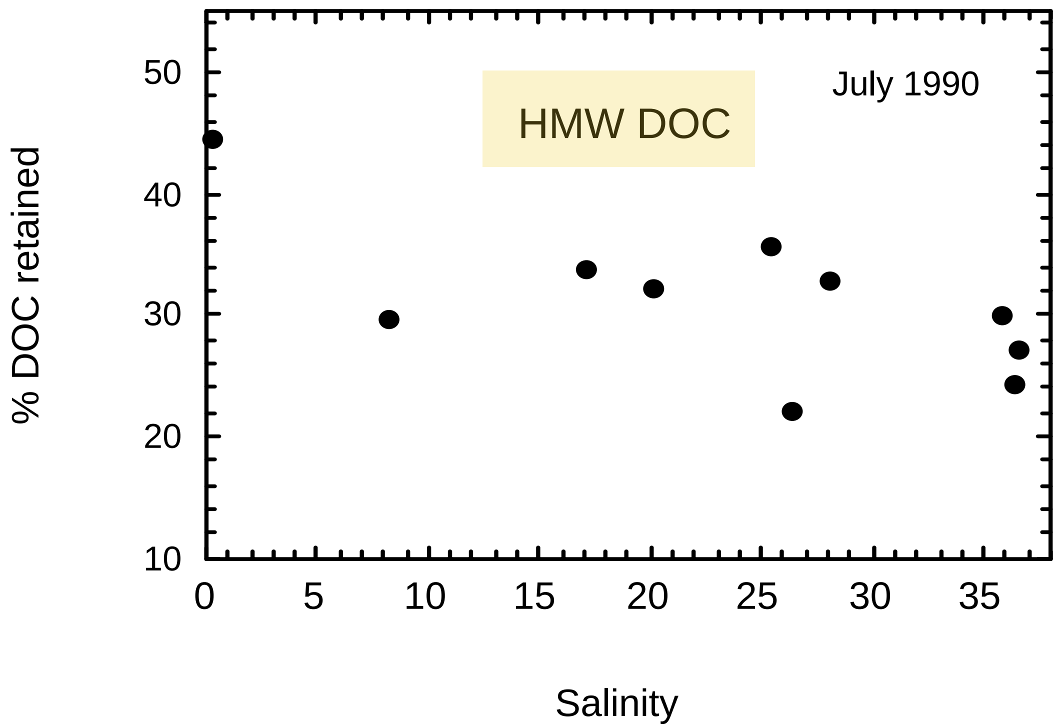
- DOC source at mid salinity where chlorophyll is high in summer
- DOC mixing is more conservative in winter when chlorophyll is low



(Benner and Opsahl, 2001)

DOM in the Mississippi River plume

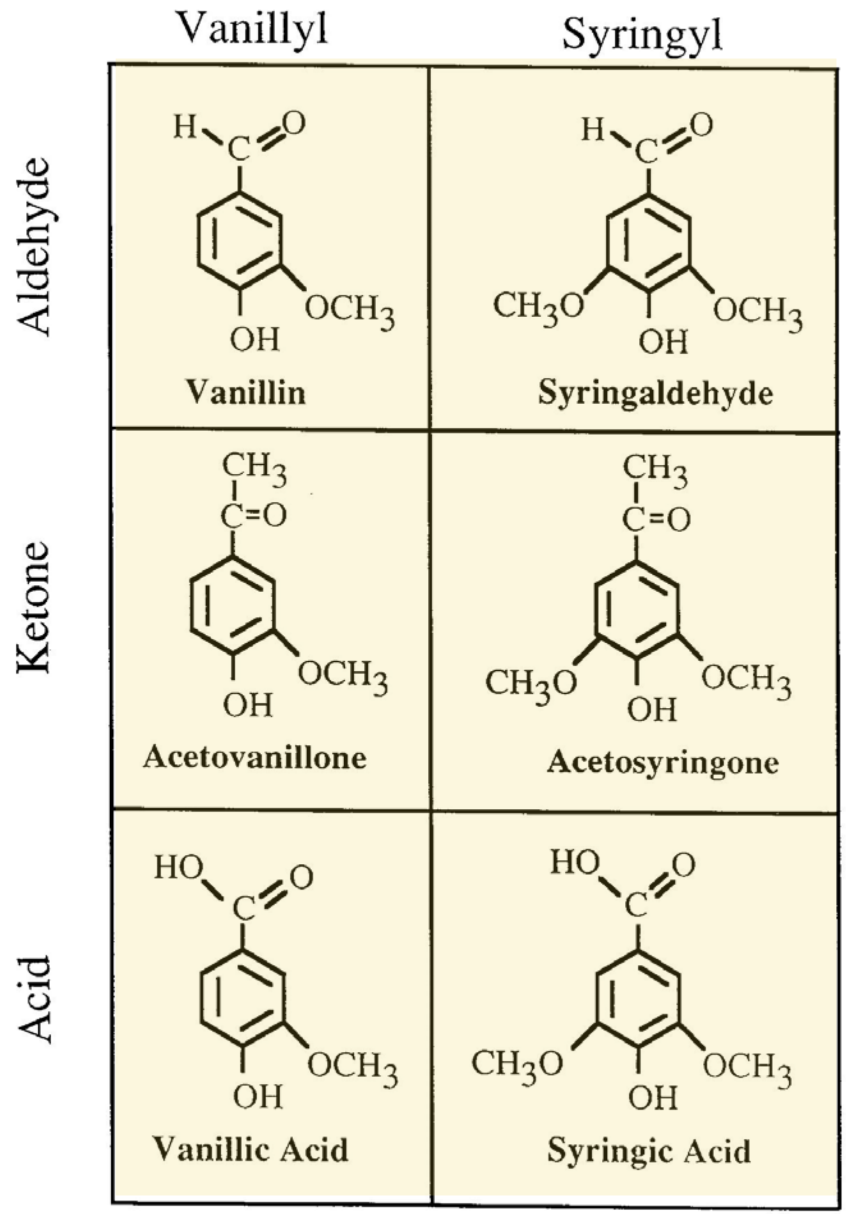
Ultrafiltered DOM concentrates (1 kDa - 0.2 µm)



Amino acids and neutral sugars are common to terrigenous and marine organisms.

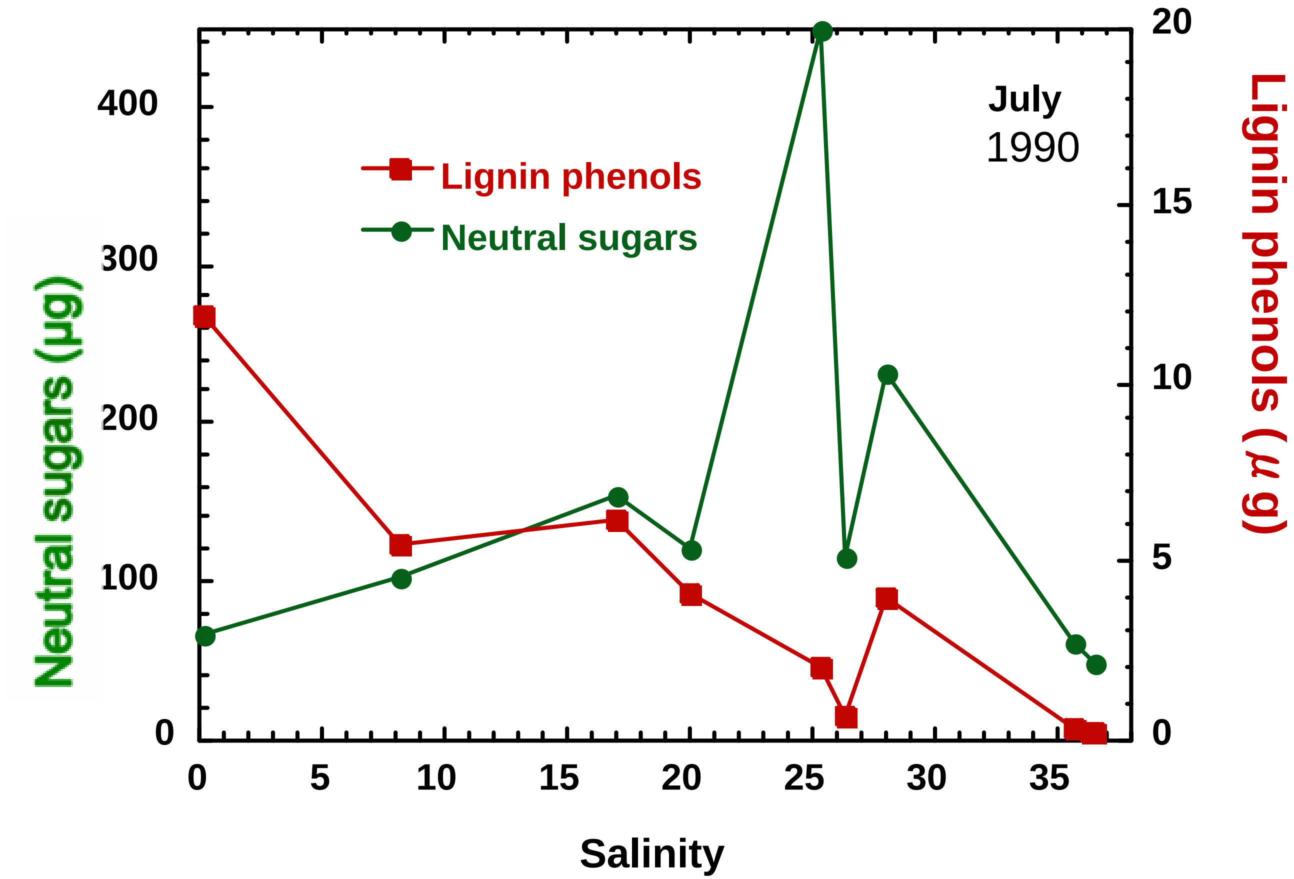
Lignin phenols (V, S) are unique to vascular plants. These biomarkers are also indicators of diagenetic alterations.

Major CuO Oxidation Products of Lignin



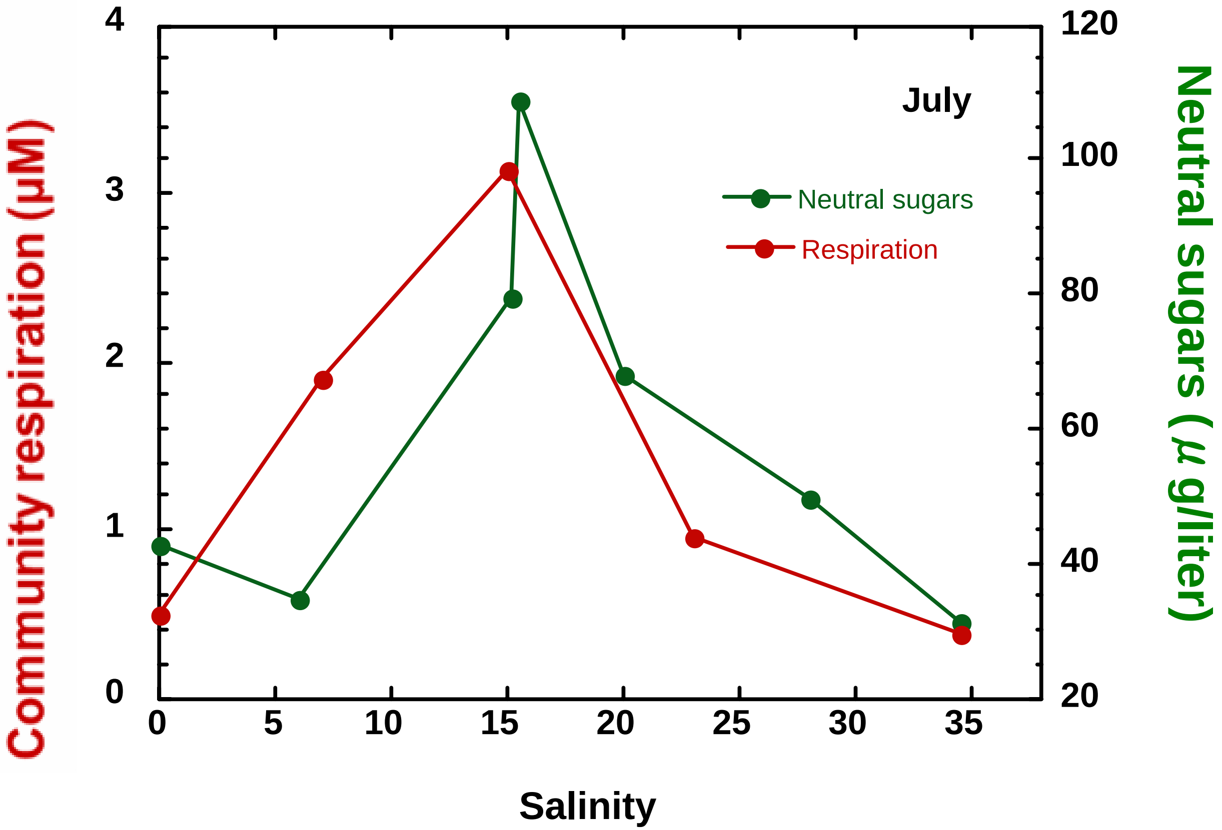
DOM in the Mississippi River plume

- neutral sugar source at mid salinity
- lignin phenol loss at low salinity



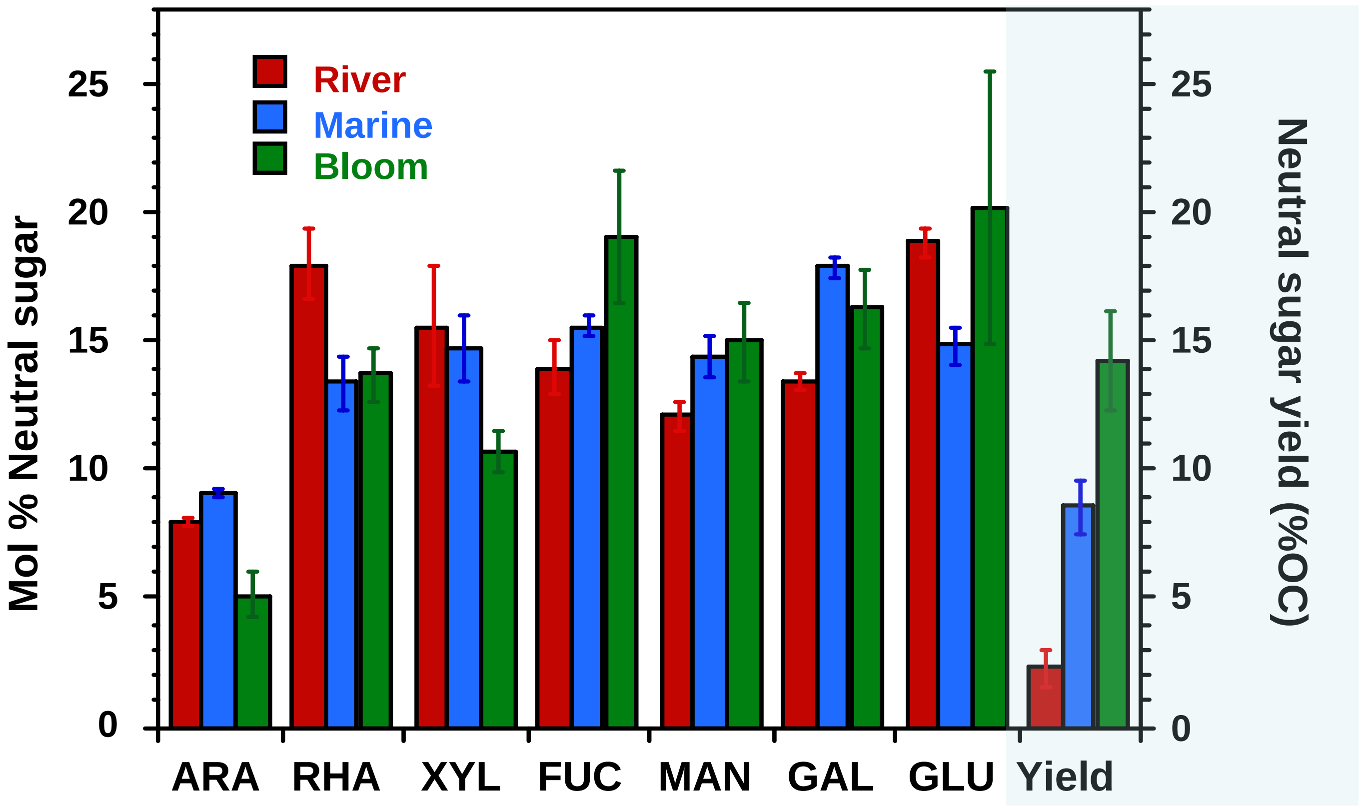
DOM in the Mississippi River plume

- plankton respiration and bacterial production are high at mid salinity
- neutral sugars are bioavailable components of DOM



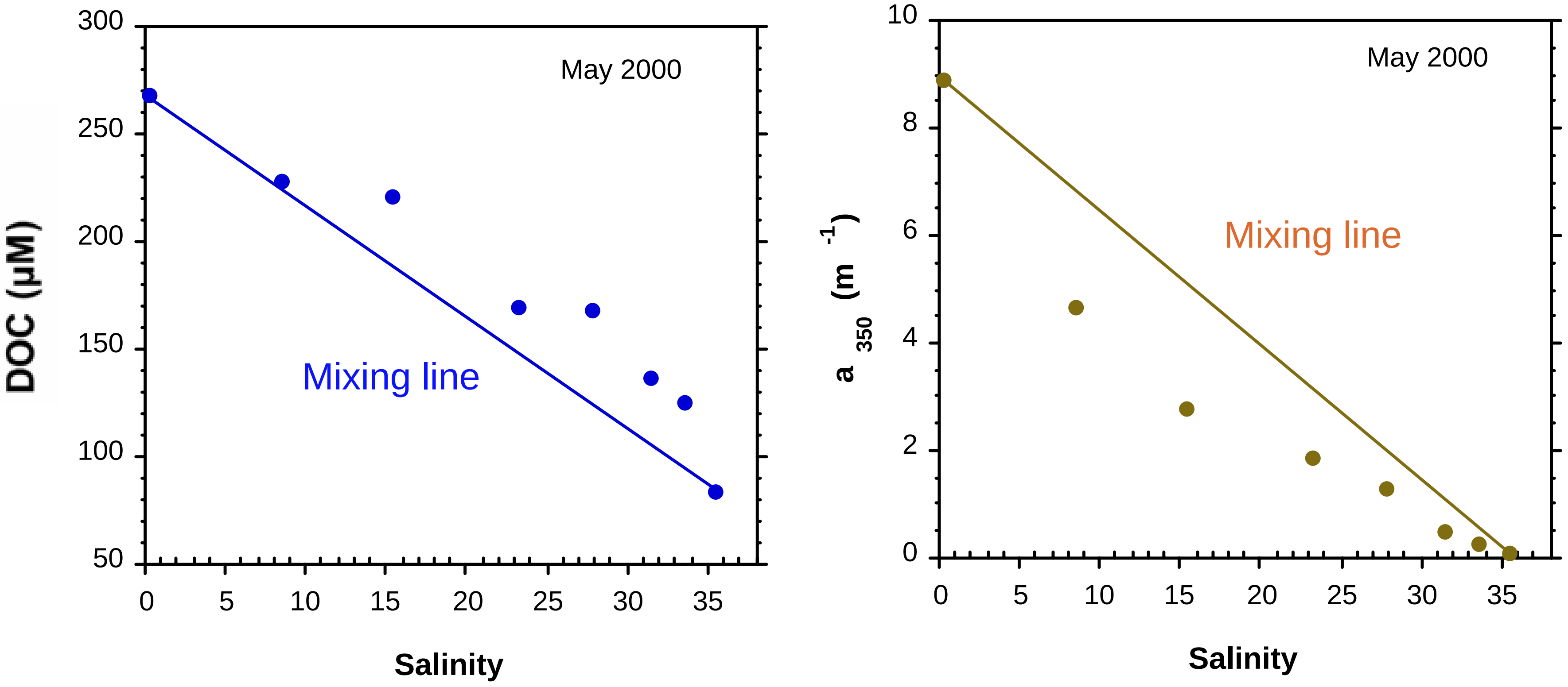
DOM in the Mississippi River plume

- composition of neutral sugars indicates heteropolysaccharides
- yields of sugars increase 6-fold from river to bloom DOM
- most neutral sugars are of autochthonous origin in the plume



DOM in the Mississippi River plume

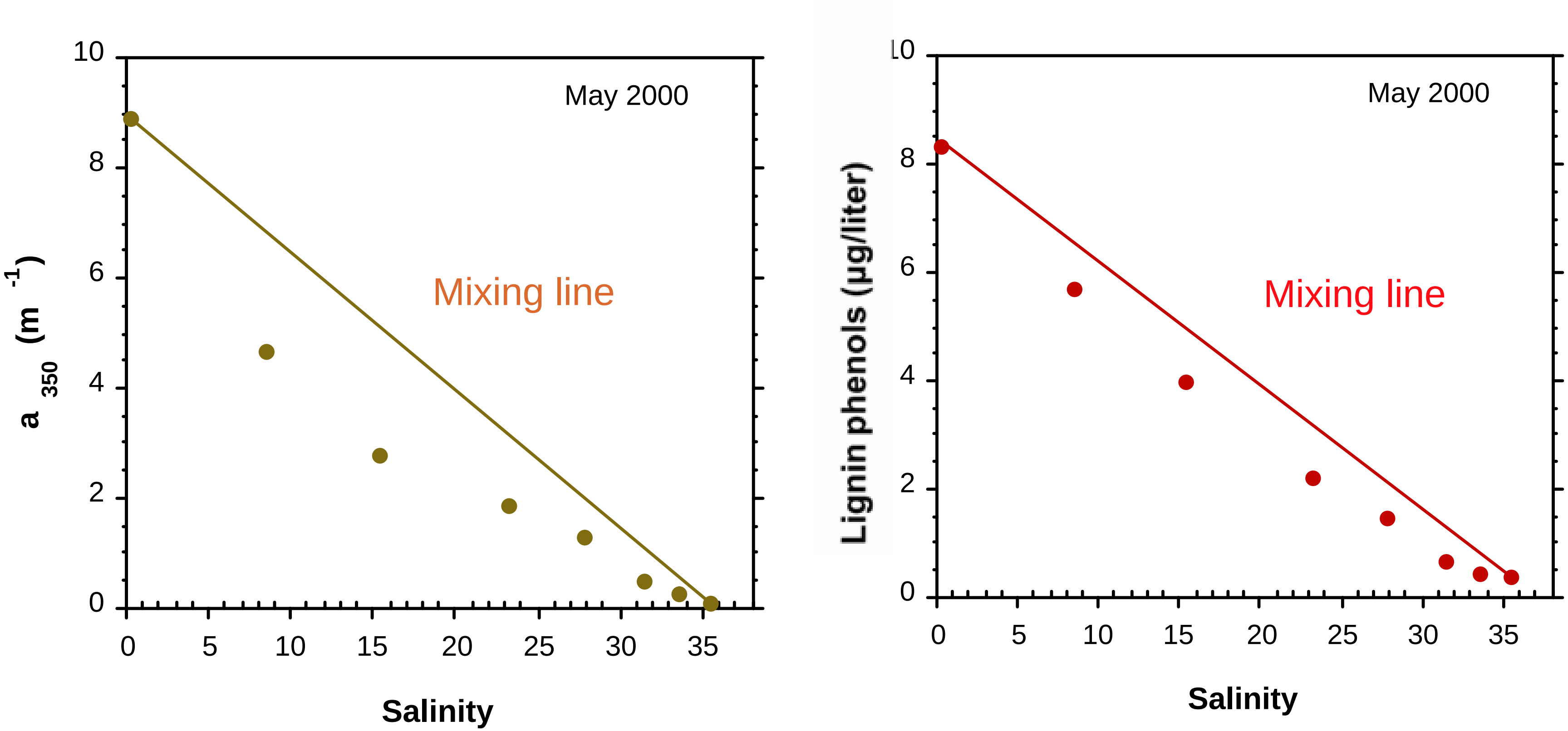
- DOC and absorption (a_{350}) follow different salinity distribution patterns
- 35% loss of absorption (a_{350}) at low salinity



(Hernes and Benner, 2003)

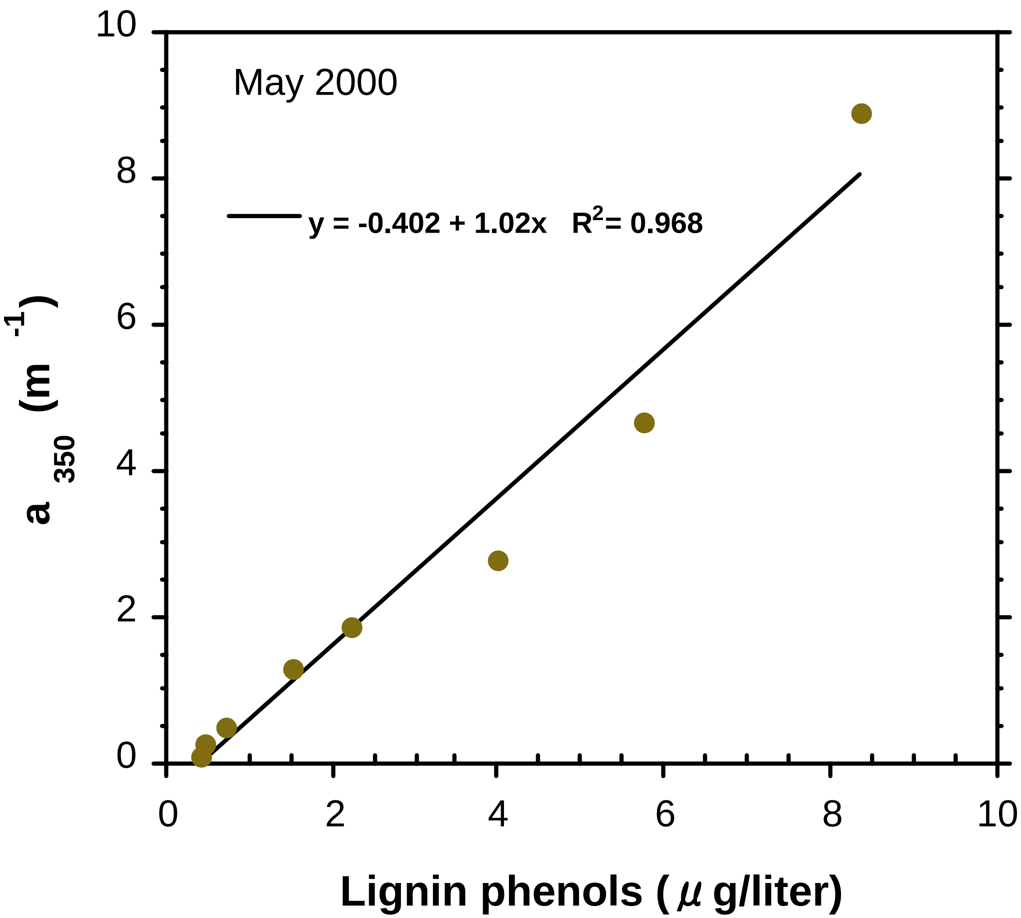
DOM in the Mississippi River plume

- absorption (a_{350}) and lignin phenols follow similar salinity distribution patterns
- 14% loss of lignin phenols at low salinity (total lignin phenols by C_{18} extraction)



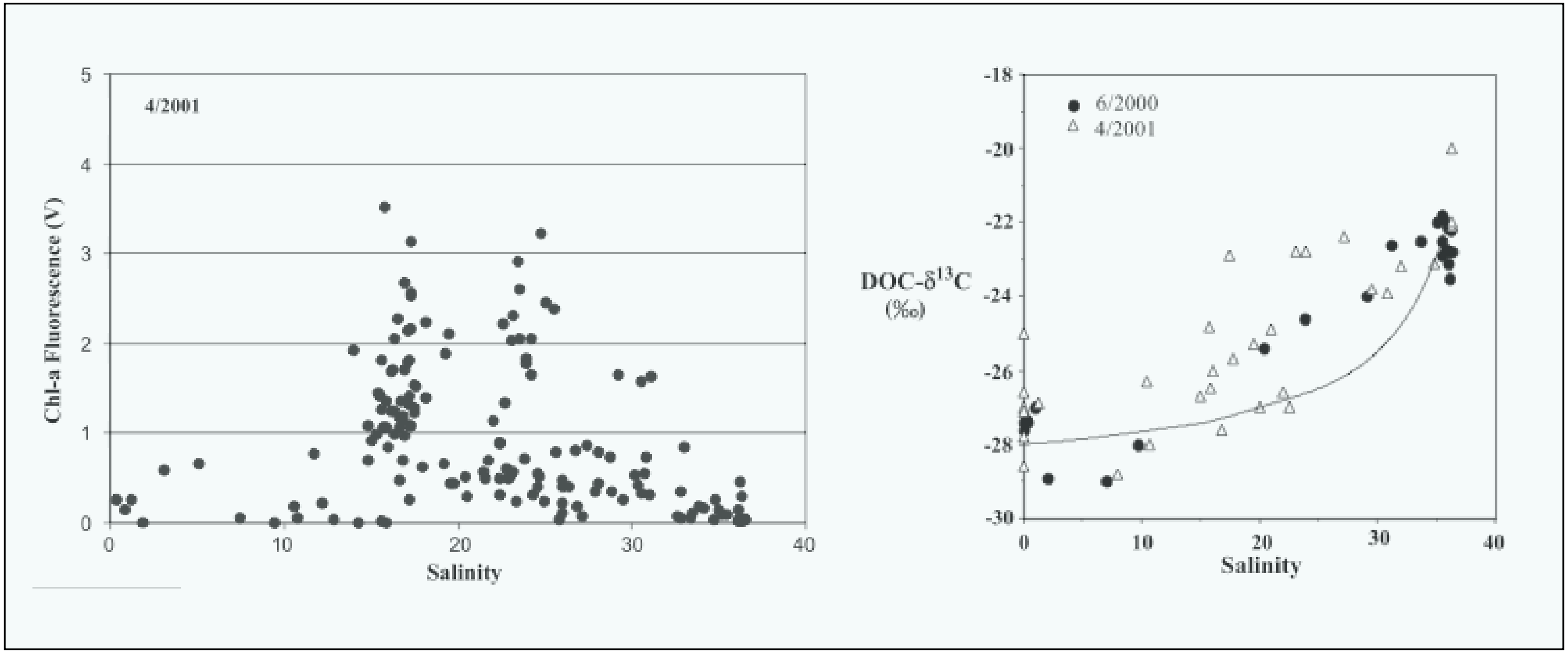
DOM in the Mississippi River plume

- absorption (a_{350}) and lignin phenol concentrations are linearly related



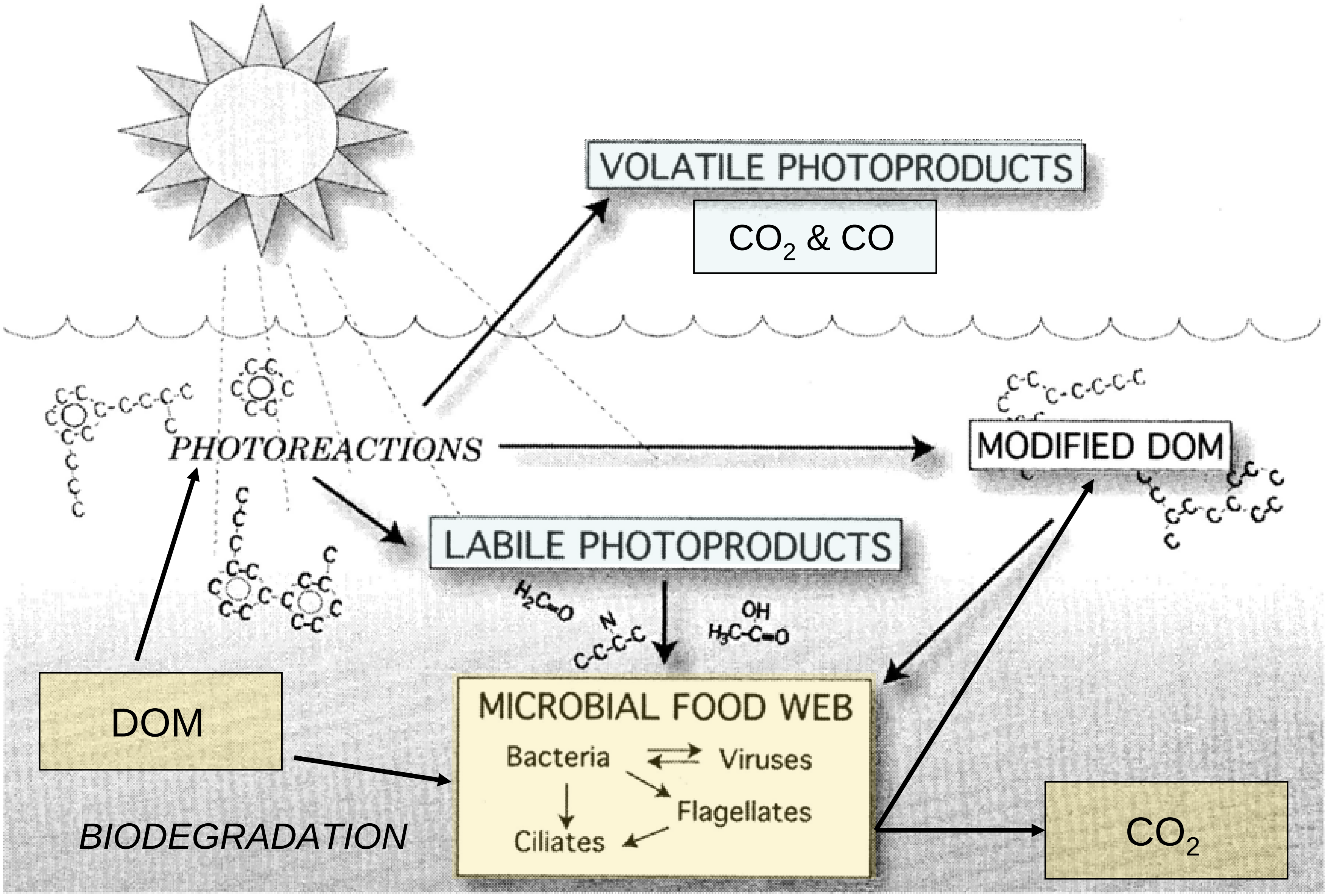
DOM in the Mississippi River plume

- DOC in mid salinity waters with high chl-a is enriched in ^{13}C
- desorption of DOC from particulates at low salinities
- variable $p^{13}CO_2$ values at mid salinities are likely



(Wang et al., 2004)

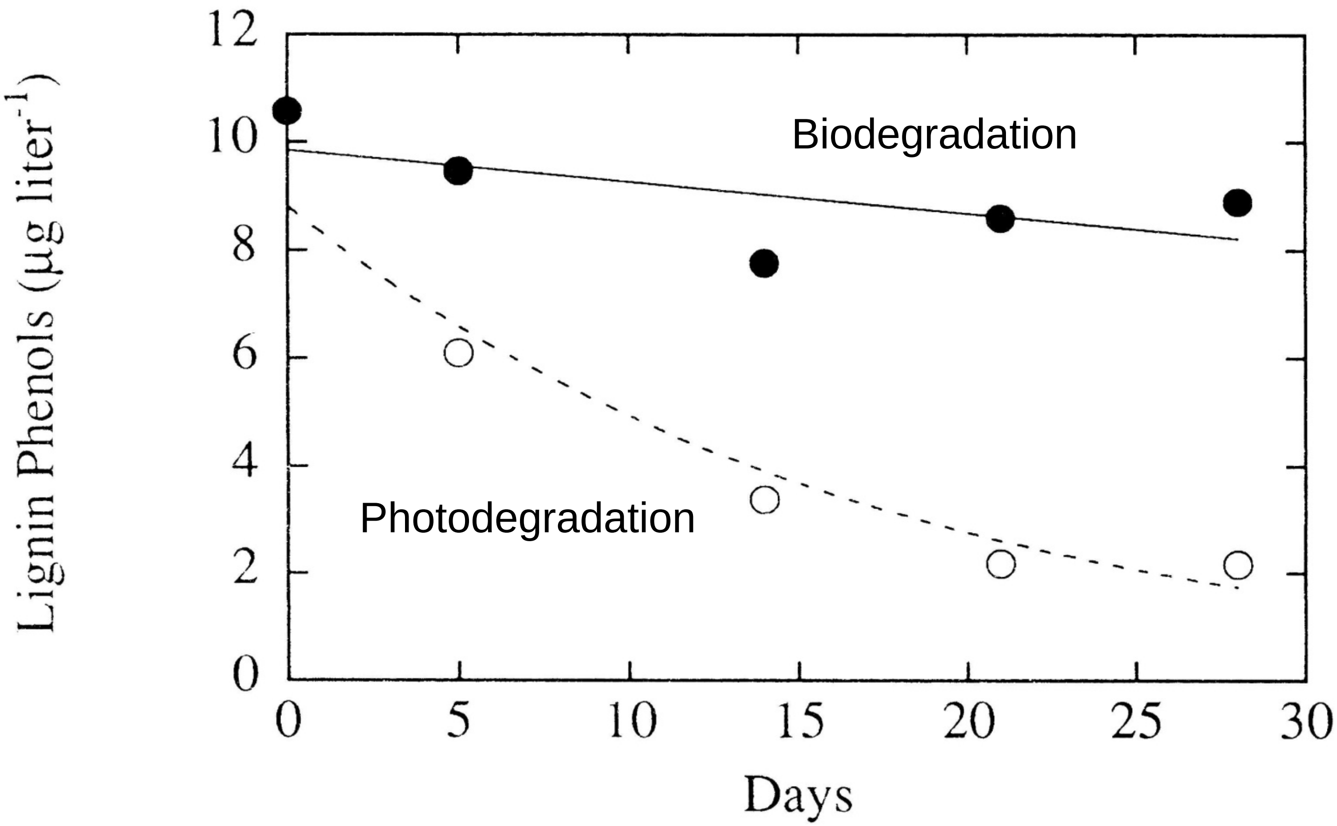
Decomposition of DOM



(modifed from Moran and Covert 2003)

Photochemical and microbial decomposition of Mississippi River DOM

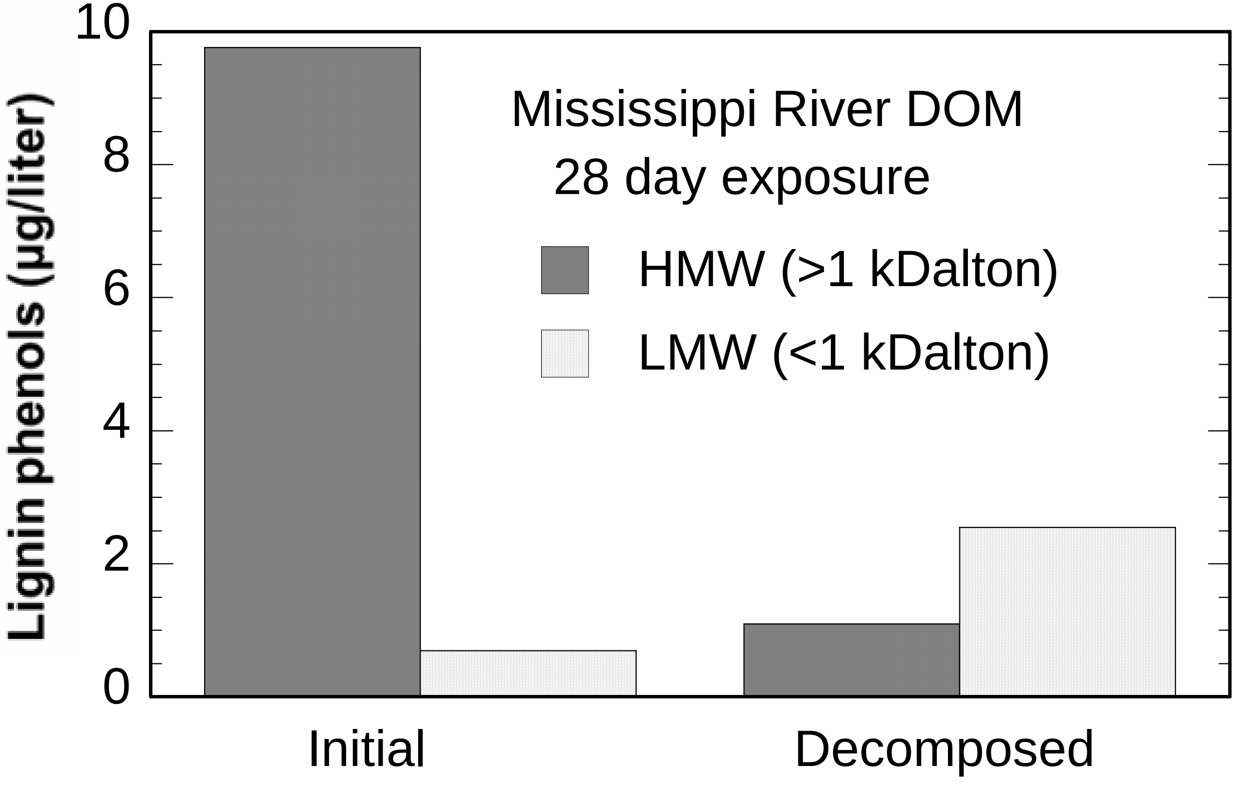
- 28 day exposure to natural sunlight
- rate of photodegradation is 5-fold greater than biodegradation



(Opsahl and Benner, 1998)

Photochemical and microbial decomposition of Mississippi River DOM

- photodegradation results in a major decrease in MW of lignin



Bio- and photo-degradation of DOM from the Broad River, SC

(GF/F filtered)

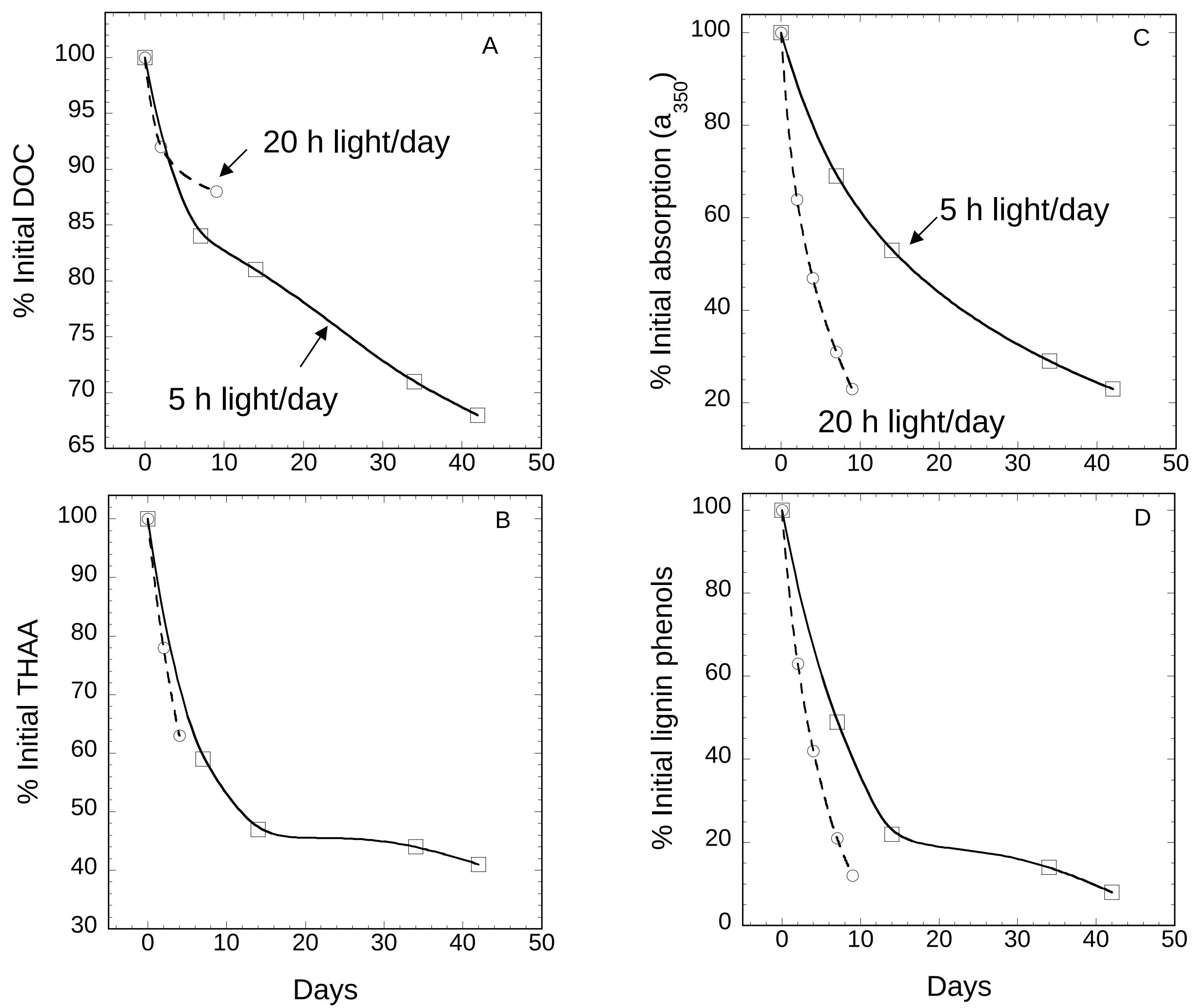
February	**May**
231 µM DOC a_{350} = 7.908	197 µM DOC a_{350} = 6.326
20 h light/day	5 h light/day
9 day treatment 257 MJ m^{-2} dose	42 d treatment 307 MJ m^{-2} dose

Suntest XLS+
Solar simulator

Samples collected periodically for DOC, a_{350} (m^{-1}), amino acids, lignin phenols

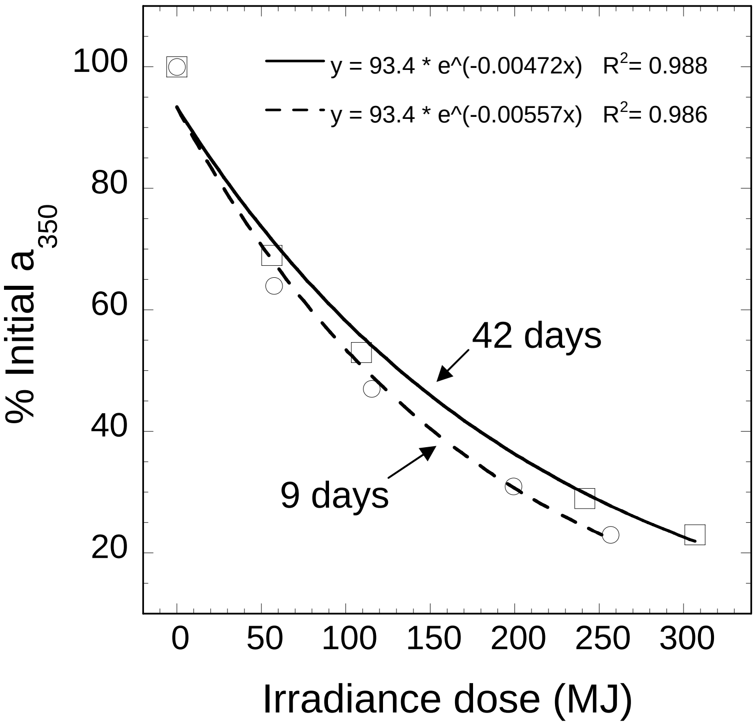
The extent of DOC and THAA losses are related to incubation time (biodegradation)

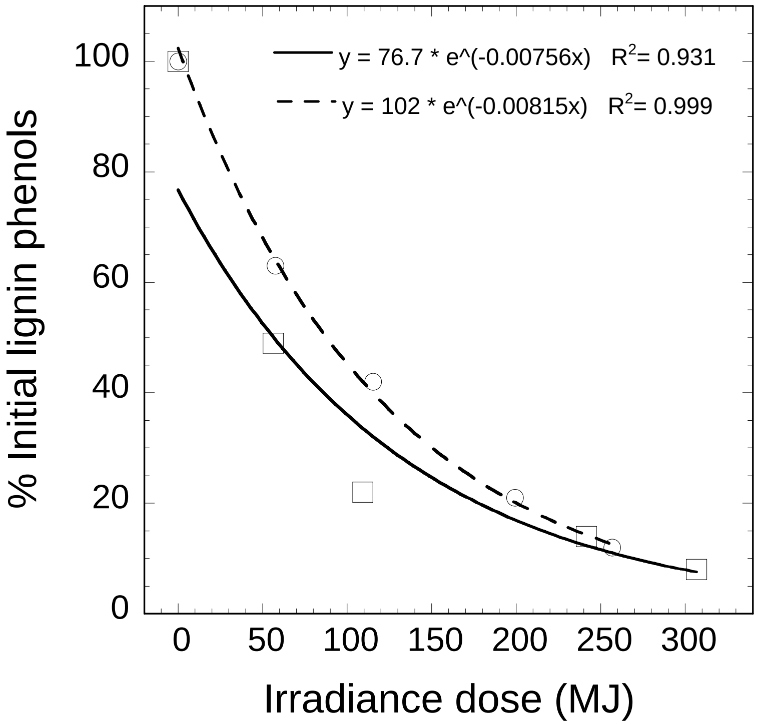
The extent of a_{350} and lignin losses are related to light exposure (photodegradation)



Bio- and photo-degradation of DOM from the Broad River, SC

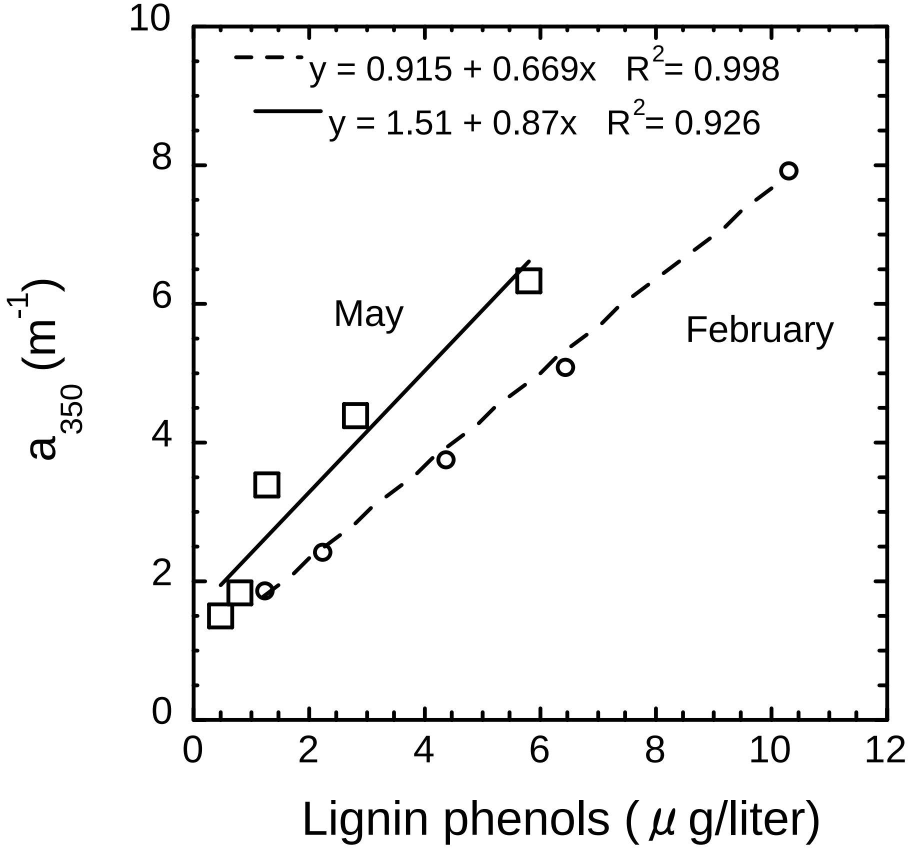
• losses of a_{350} and lignin phenols are largely due to photodegradation





Bio- and photo-degradation of DOM from the Broad River, SC

- absorption (a_{350}) is linearly related to lignin phenol concentrations

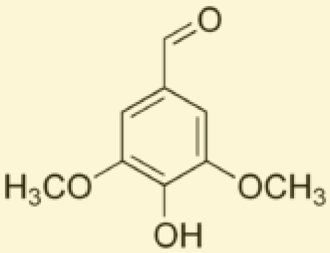


The large difference in the initial lignin phenol concentrations between Feb and May is not reflected in a_{350} indicating lignin is not the dominant chromophore. However, the dominant chromophores are of similar photoreactivity as lignin.

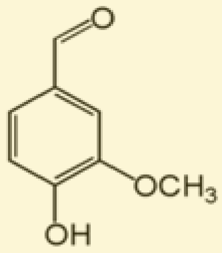
Bio- and photo-degradation of DOM from the Broad River, SC

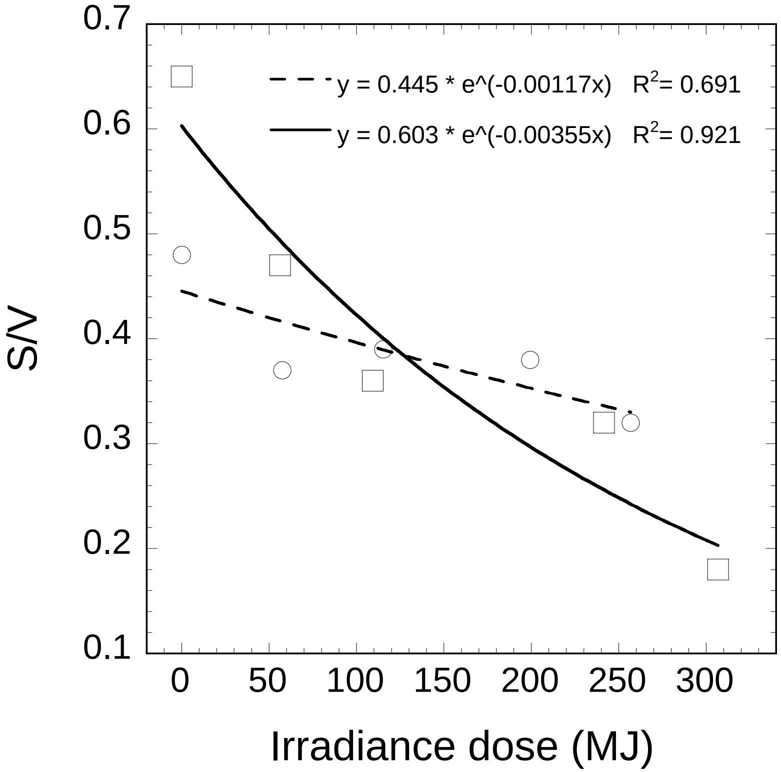
- compositional differences in lignin affect photodegradation and a_{350}

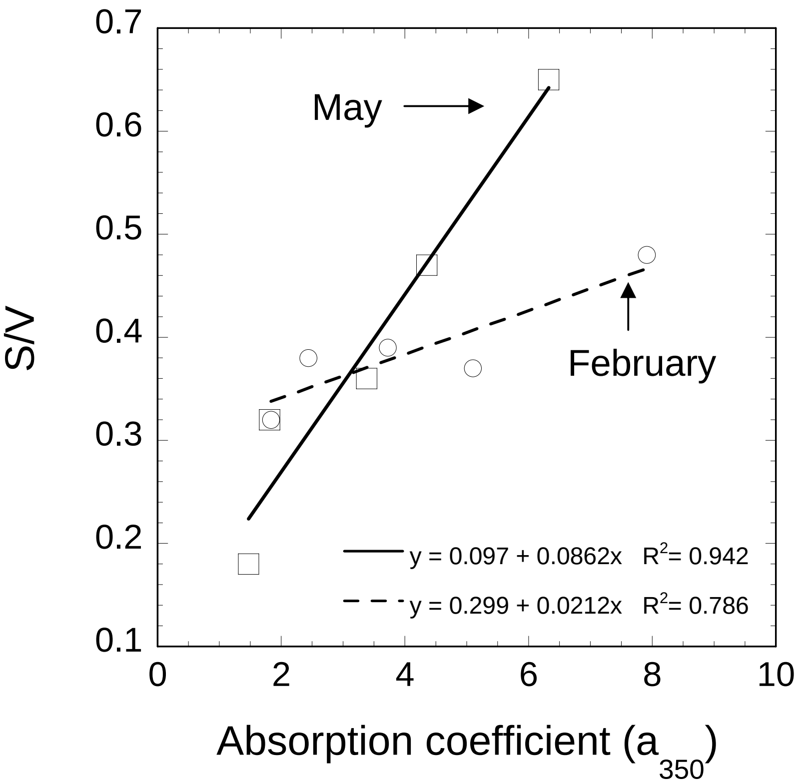
Syringaldehyde (S)



Vanillin (V)

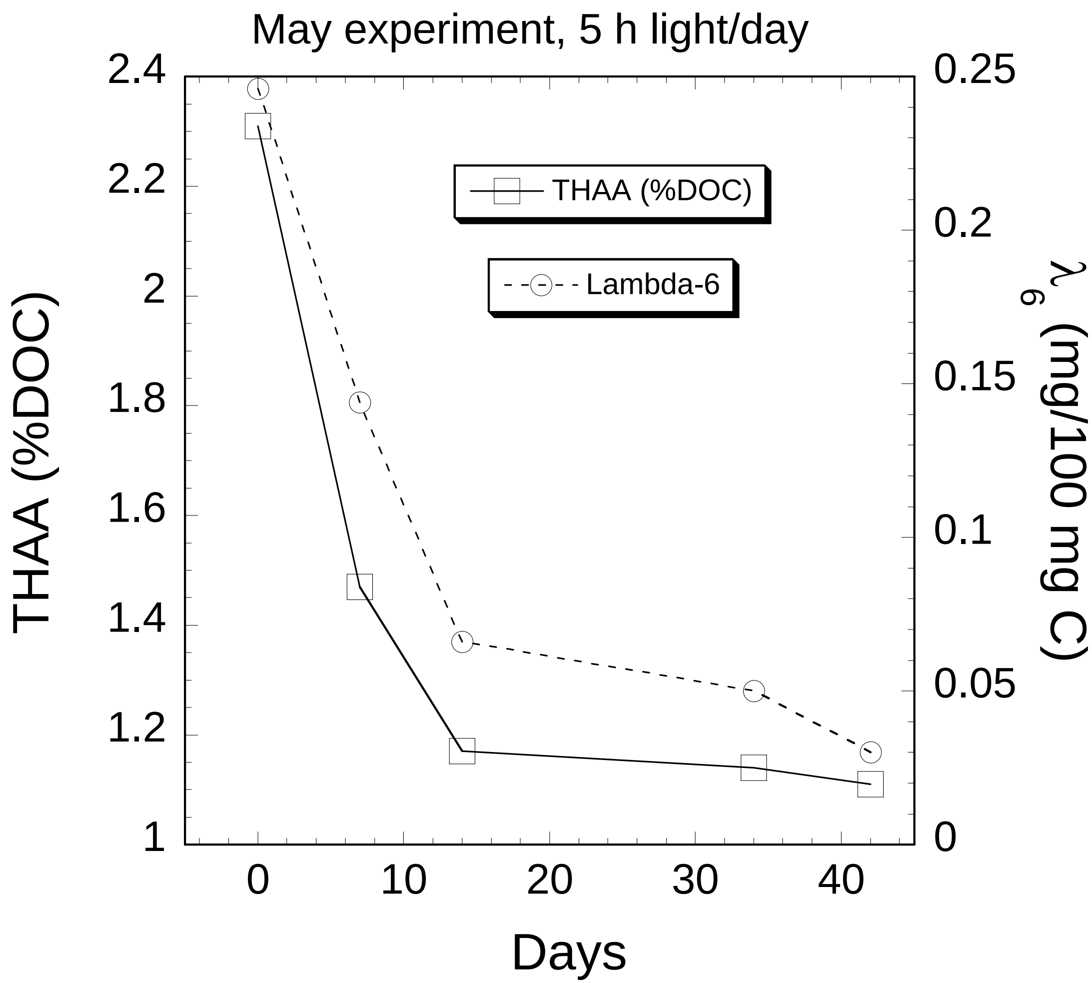






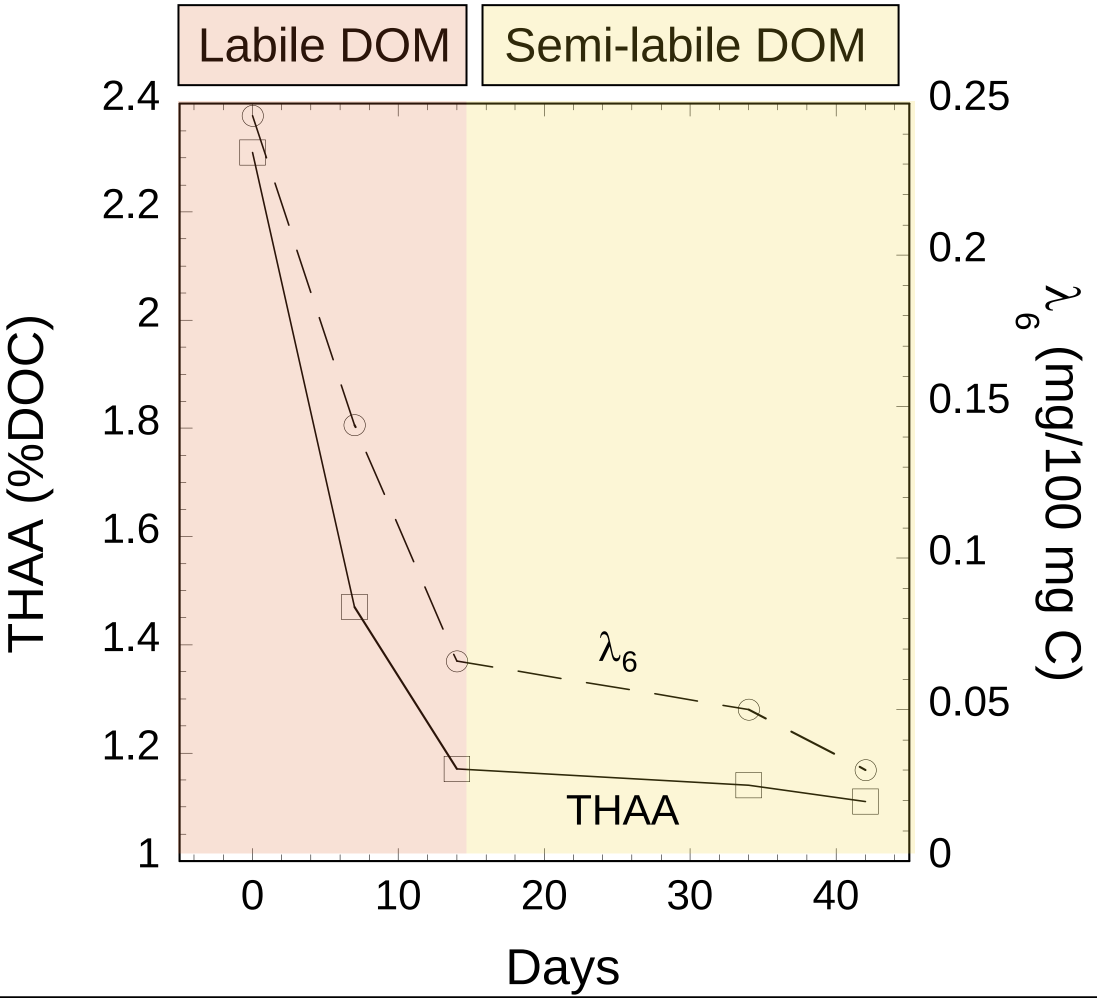
Bio- and photo-degradation of DOM from the Broad River, SC

- bio- and photo-degradation are chemically selective



Bio- and photo-degradation of DOM from the Broad River, SC

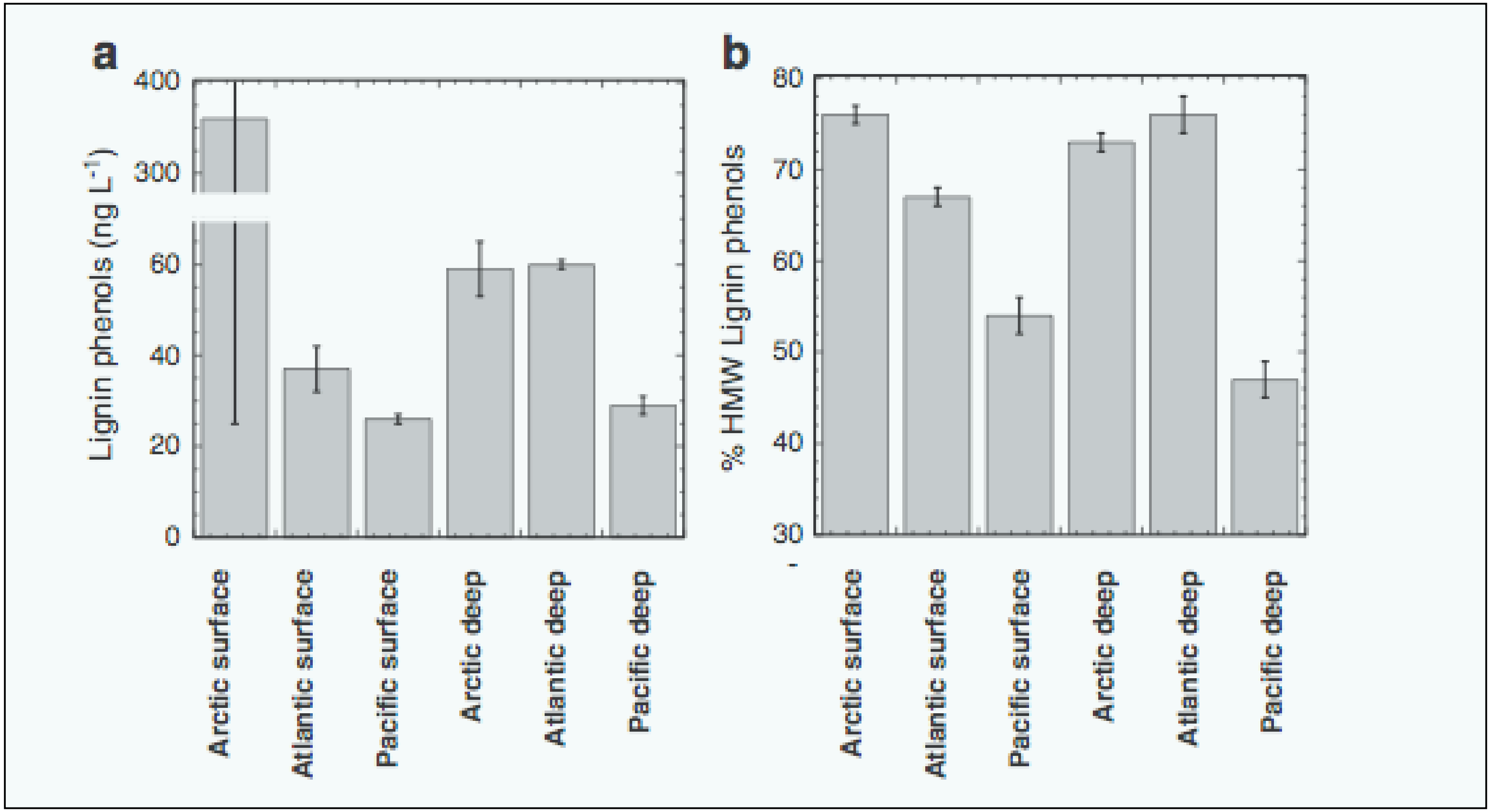
- the initial yield of THAA is indicative of DOM bioavailability
- the initial yield of lignin phenols is indicative of DOM photoreactivity



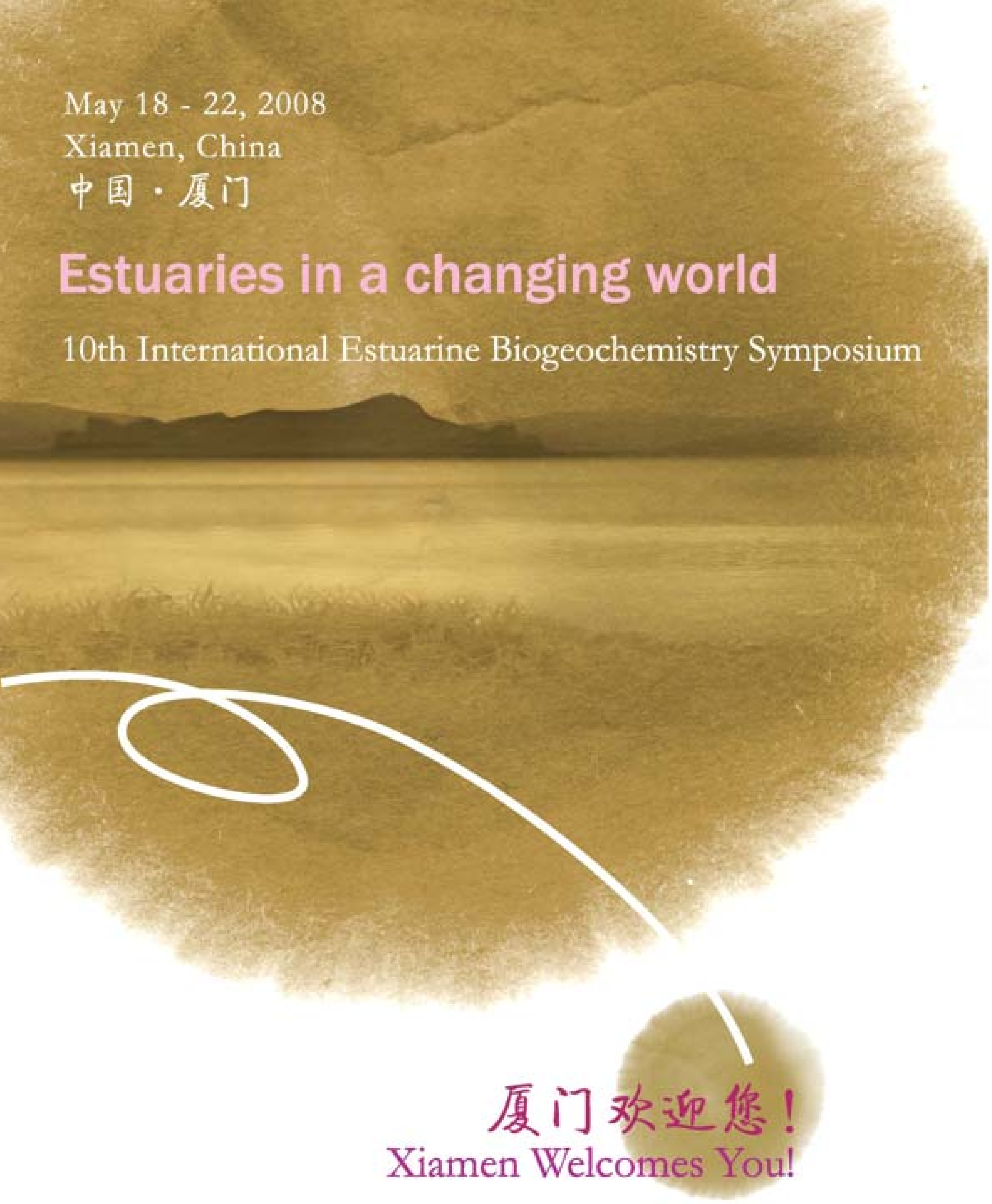
18.8% (37 µM) of DOC is labile when both bio- and photo-degradation are considered

Global ocean distribution of terrigenous DOM

- the concentrations and MW distributions of lignin phenols are consistent with patterns of global riverine discharge and photochemical-microbial transformations and remineralization



(Hernes and Benner, 2006)



Xie Xie
Prof. Minhan Dai
for organizing this
symposium

Questions?