Stochastic Synthesis of Natural Organic Matter

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Current models of NOM

Single-purpose

Carbon cycling, metal complexation, light absorption

Equations parameterized w/NOM data

$k_{consumption}$, K_{CuL}, etc.

NOM treated as pools or fractions

labile, non-chromophoric, polysaccharide

"Ideal" model of NOM

Multi-purpose

Single model for all observables

Parameterized from known molecules

Physical properties, reaction k's and)G^0

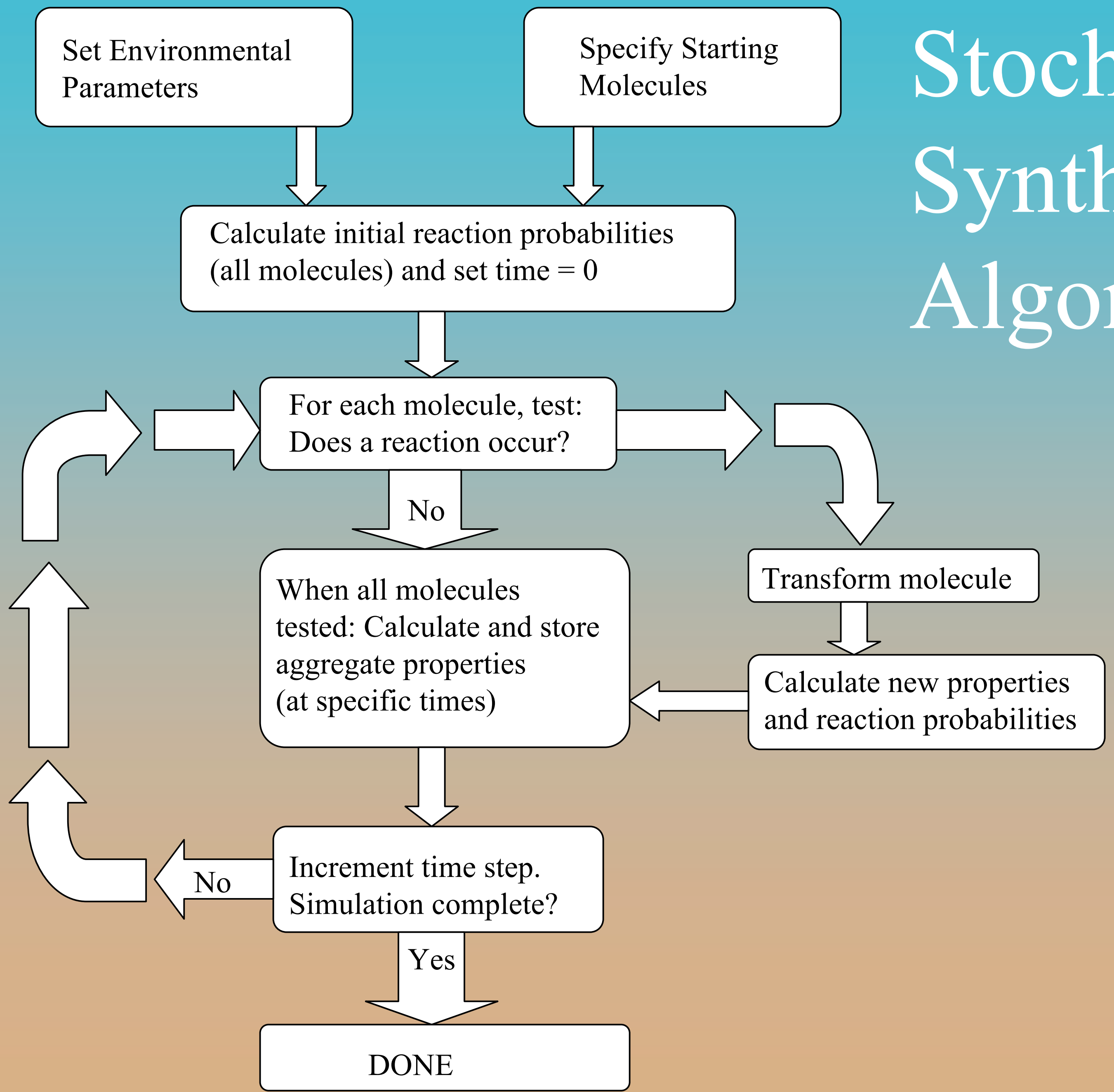
NOM treated as individual molecules

Each molecule can be different; highly complex mix

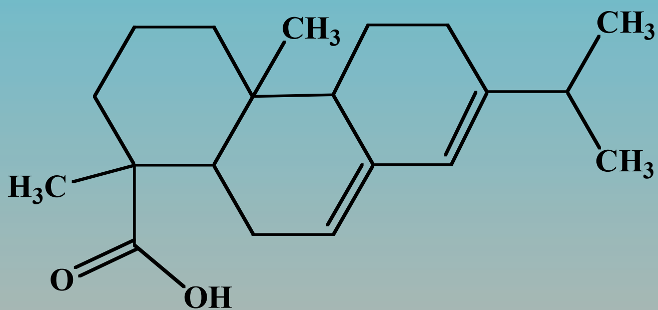
Agent-based Stochastic Synthesis Forward modeling of NOM Evolution

- Agent-based- uses individual molecules, not carbon ‘pools’- heterogeneous assemblages
- Forward modeling from precursor molecules and specific reactions- no ‘fitted’ parameters
- No constraints on types of NOM molecules- no ‘pre-conceived’ structures
- Calculates individual and ensemble properties- can be compared to analytical data or used to examine individual structures

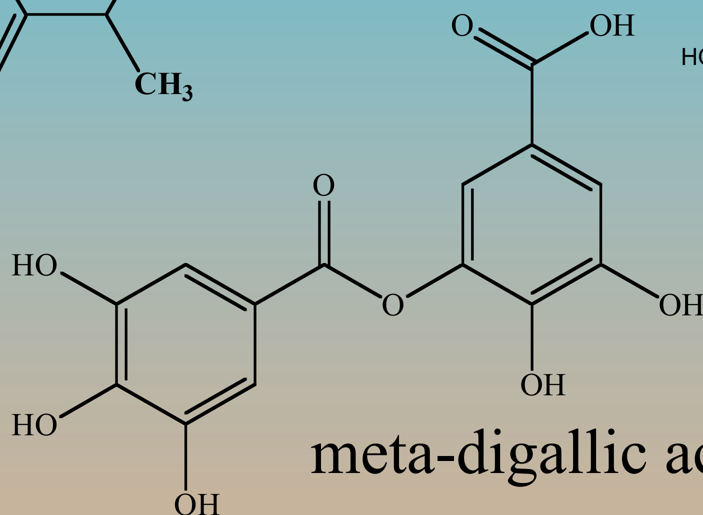
Stochastic Synthesis: Algorithm



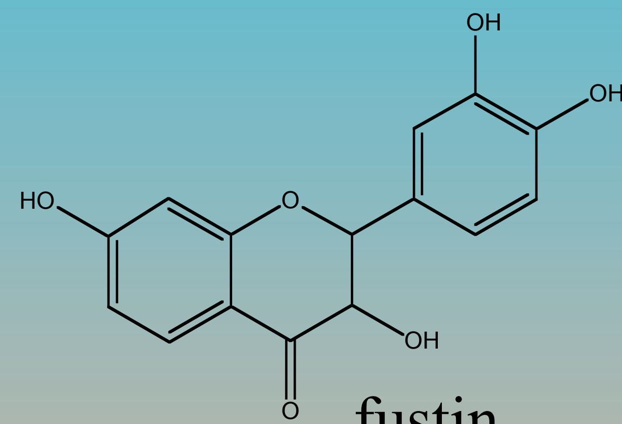
Can we convert terpenes, tannins and flavonoids in soil into NOM ?



abietic acid



meta-digallic acid



fustin

2000 molecules each

Atmospheric O_2 (0.3 mM) — Acidic pH (5.0)

High oxidase activity (0.1) — ~5.5 months

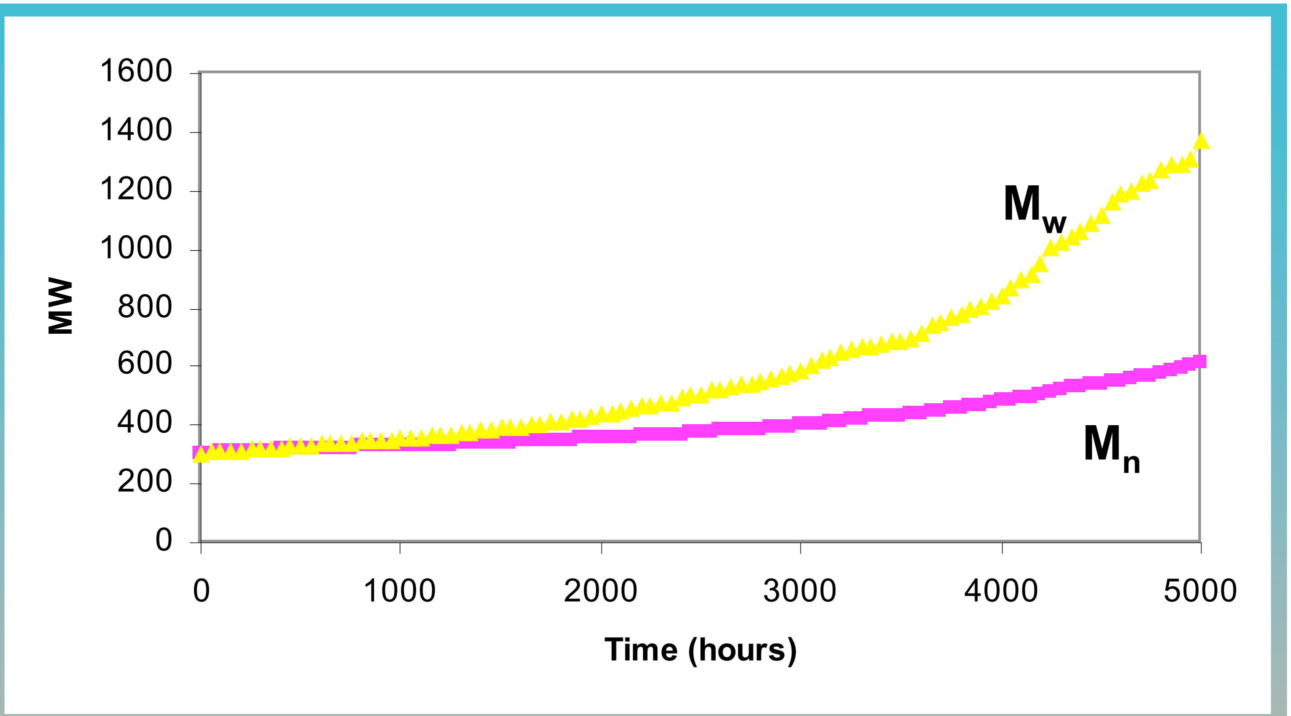
Bacterial density 0.01 — dark

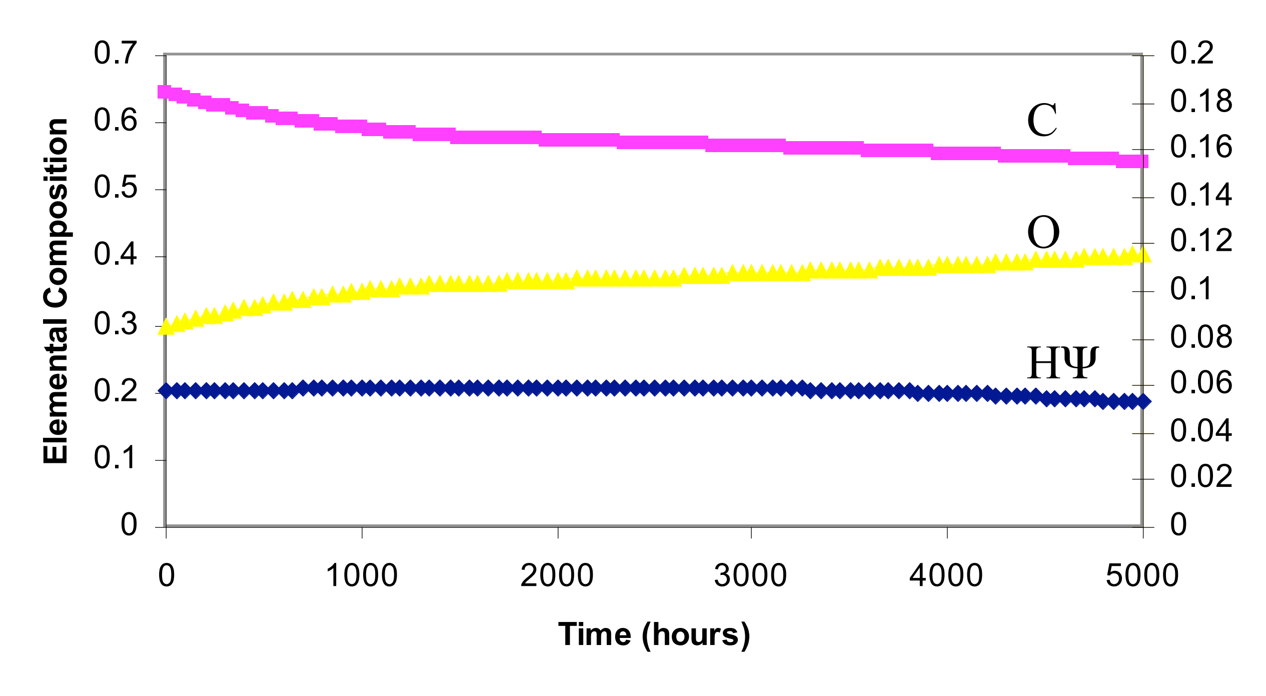
Evolution of NOM from small natural products in oxic soil

Final M_n = 612 amu,

M_w = 1374 amu

54% C, 5% H, 41%O



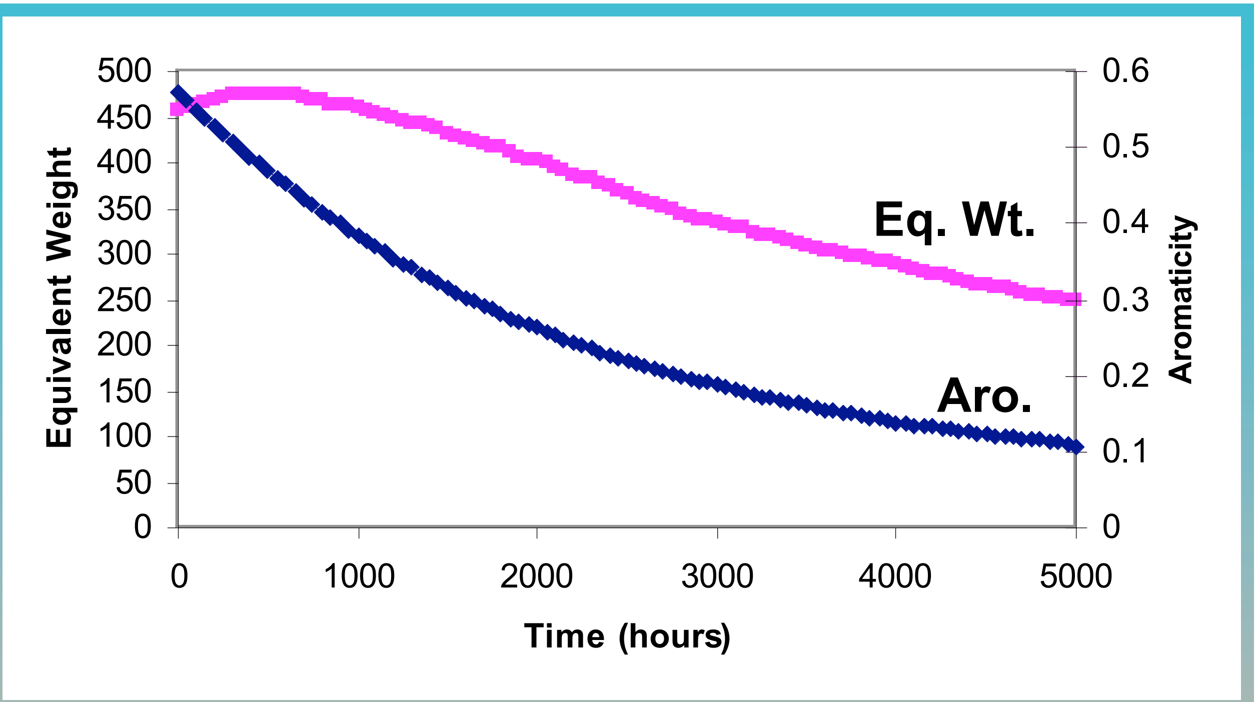


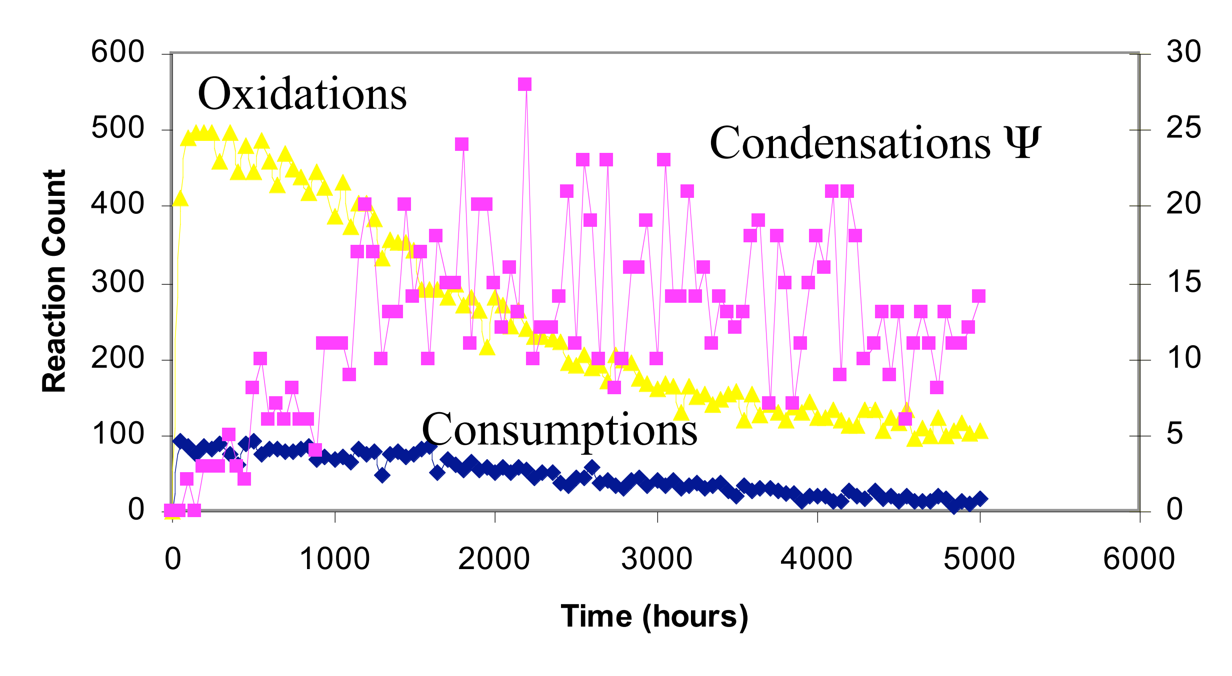
Evolution of NOM from small natural products in oxic soil

Final

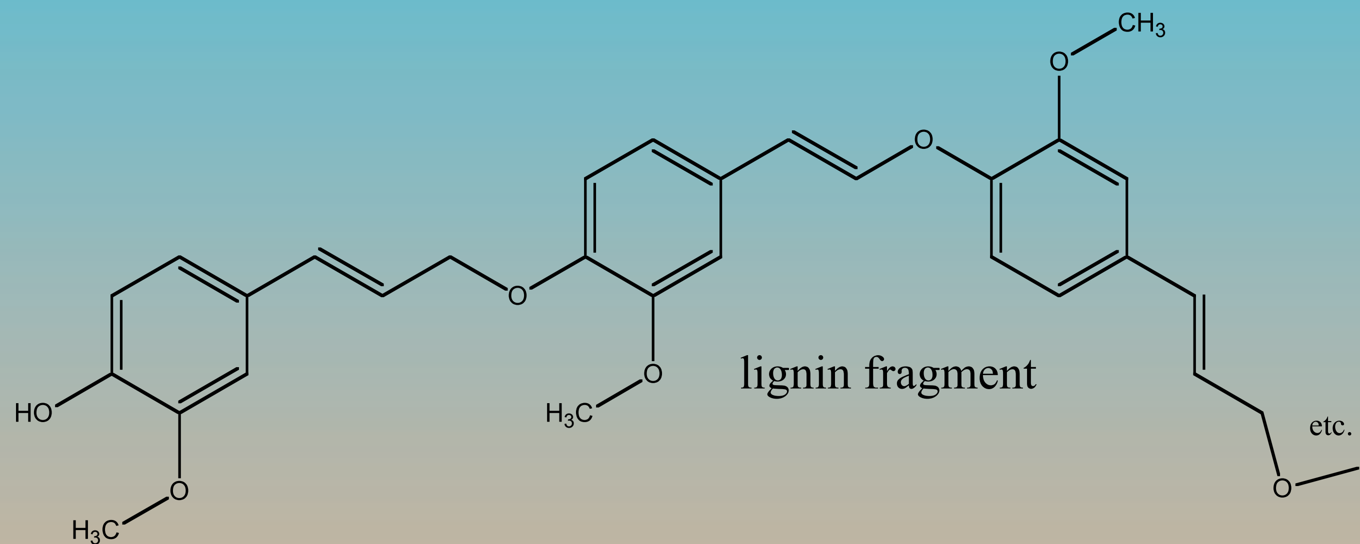
Eq. Wt. = 247 amu,

Aromatic C 11%





Trial: Can we convert lignin and protein molecules into NOM ?



Atmospheric O_2 (0.3 mM)

Neutral pH (7.0)

Lower enzyme activity (0.01)

4 months reaction time

Moderate light (2x10^{-8} E cm^{-2} hr^{-1}

24.8 ^{o}C

Moderate bacterial density (0.02)

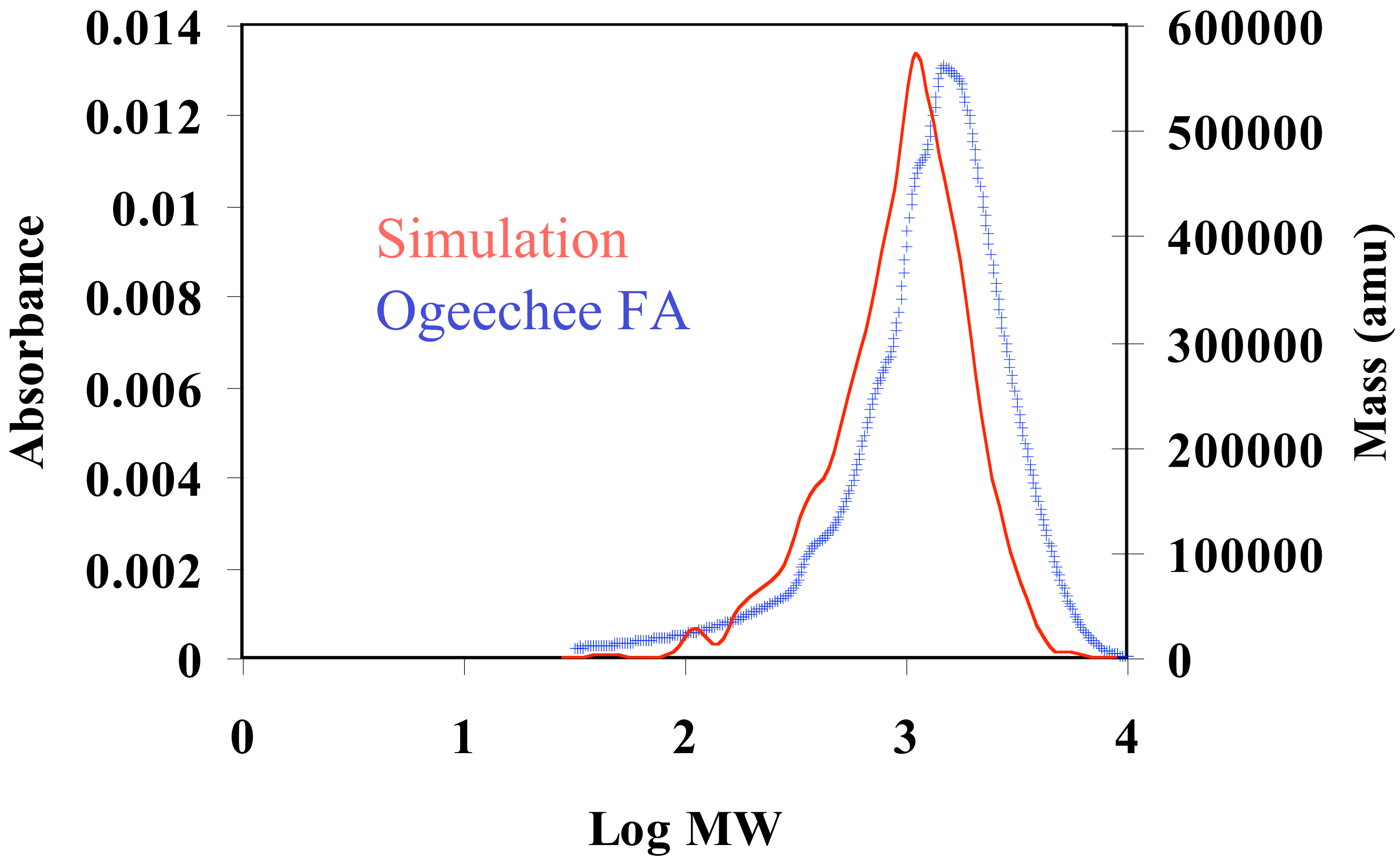
400 molecules lignin and protein

Simulated results lie within range of field measurements

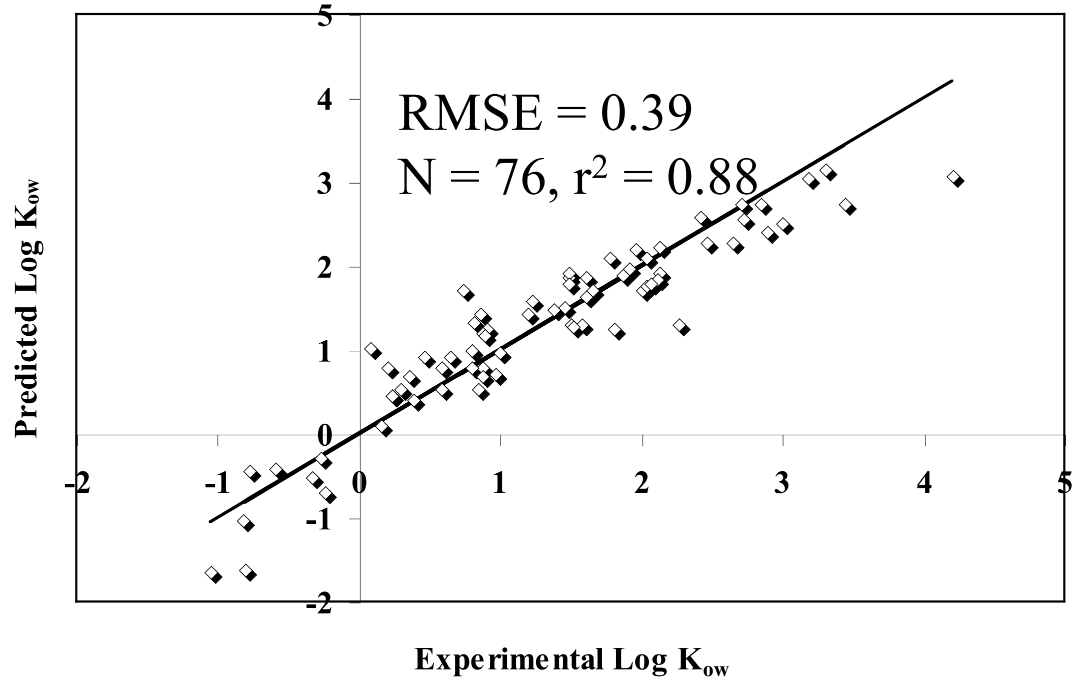
Property	Literature* Range	Simulation Results Soil	Simulation Results Surface Water
%Carbon	42%-57%	54%	44%
%Oxygen	34%-53%	41%	49%
%Hydrogen	3.6%-7.9%	5.3%	5.1%
%Nitrogen	0.4%-5.4%	-	2.3%
Mn (amu)	400-2700	612	717
Mw (amu)	784-3320	1374	1173
% Aromatic C	10%-43%	11%	10%
mEq -COOH per g	2.7-10.0	4.0	1.8

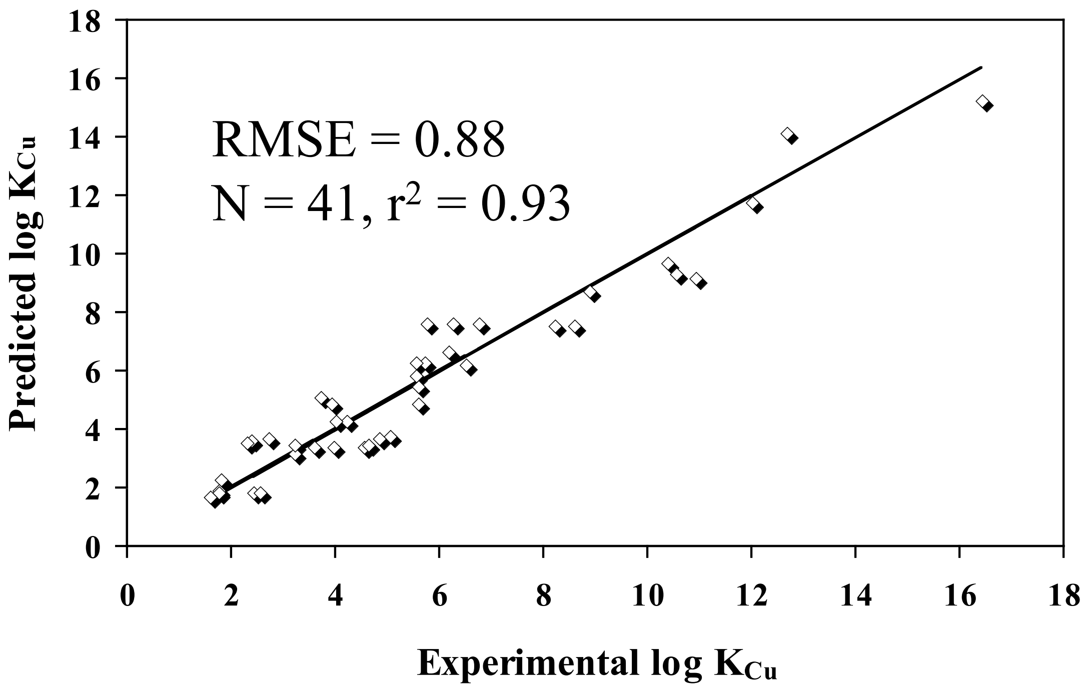
* Perdue and Ritchie (2004).

MW Distribution: Comparison w/ SE-HPLC



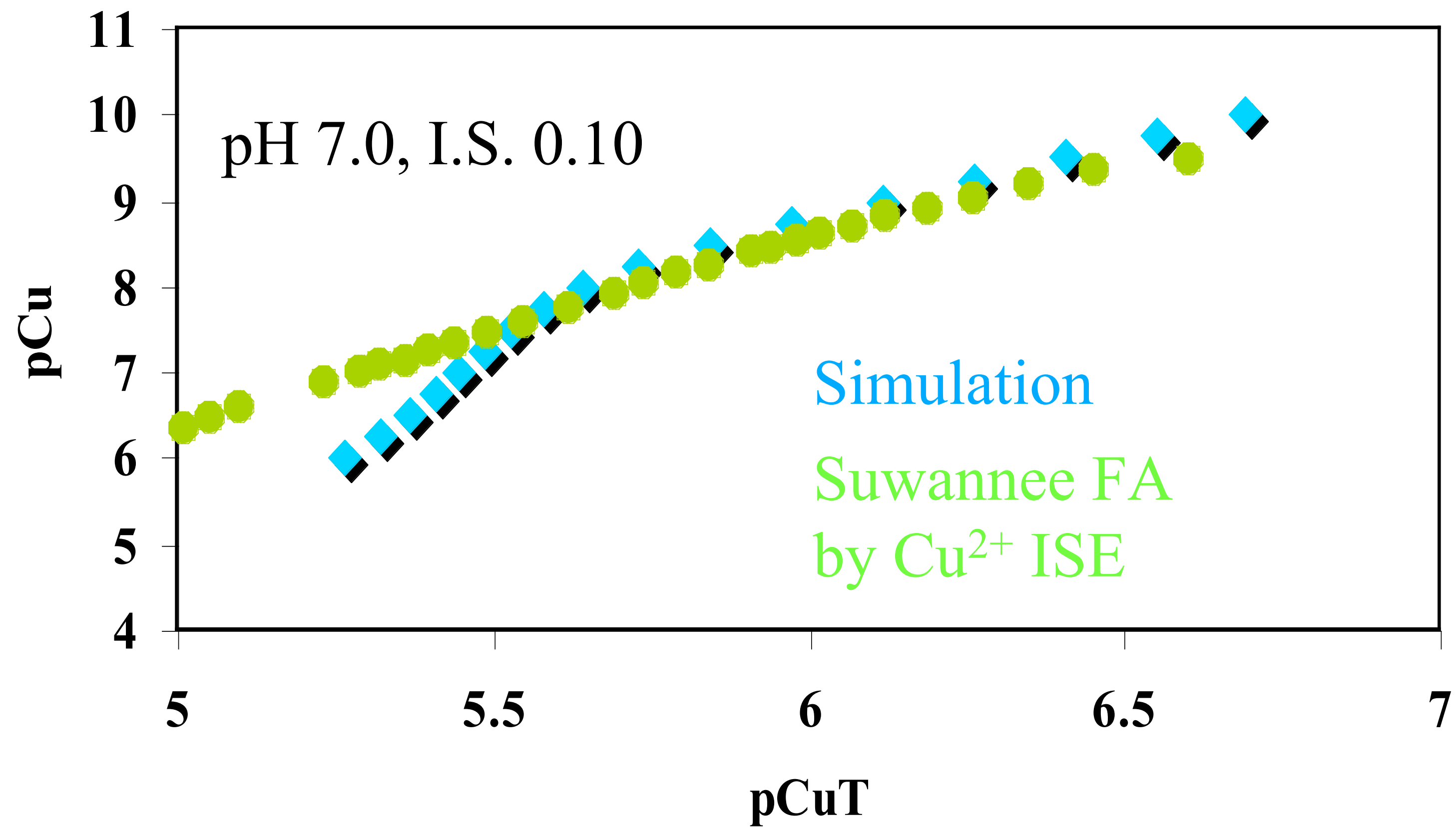
QSAR predictions of K_{Cu}, K_{ow}





Using only elemental composition and functional group counts

Predicting Cu(II) Complexation



10 mg C/L soil NOM, 1:1 binding only, K_{Cu} by QSAR

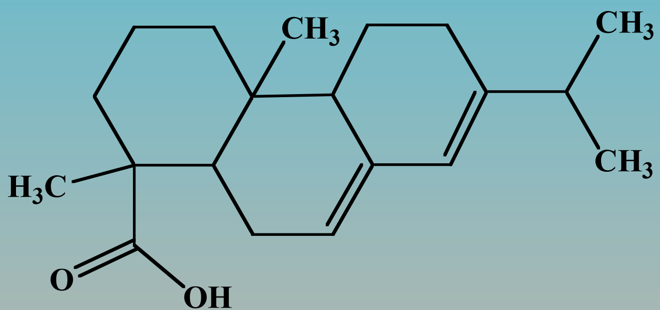
Ecological Application: Photo-labile NOM

An NOM assemblage is 'created' using
the low-oxygen soil incubation simulation.

This assemblage is exposed to surface water conditions (high O_2, pH 7, low oxidase activity) in the presence and absence of bright light (1.0×10^{-6} E hr^{-1} cm^{-2}).

Consumption of C by bacteria is compared.

How is this conversion to NOM affected by lowering the O_2 and oxidase levels?



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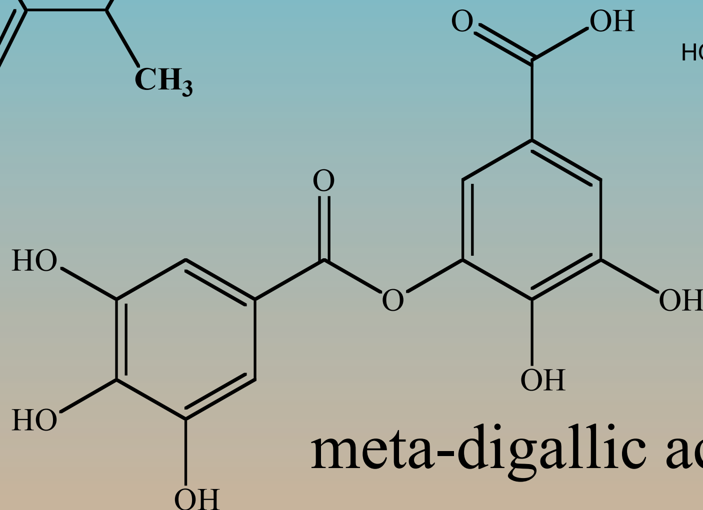

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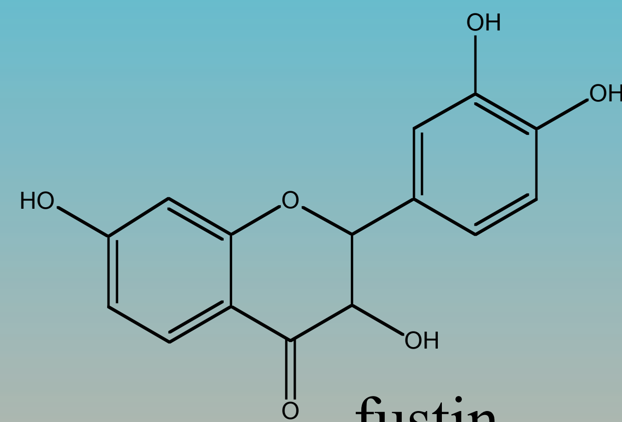


fustin

2000 molecules each

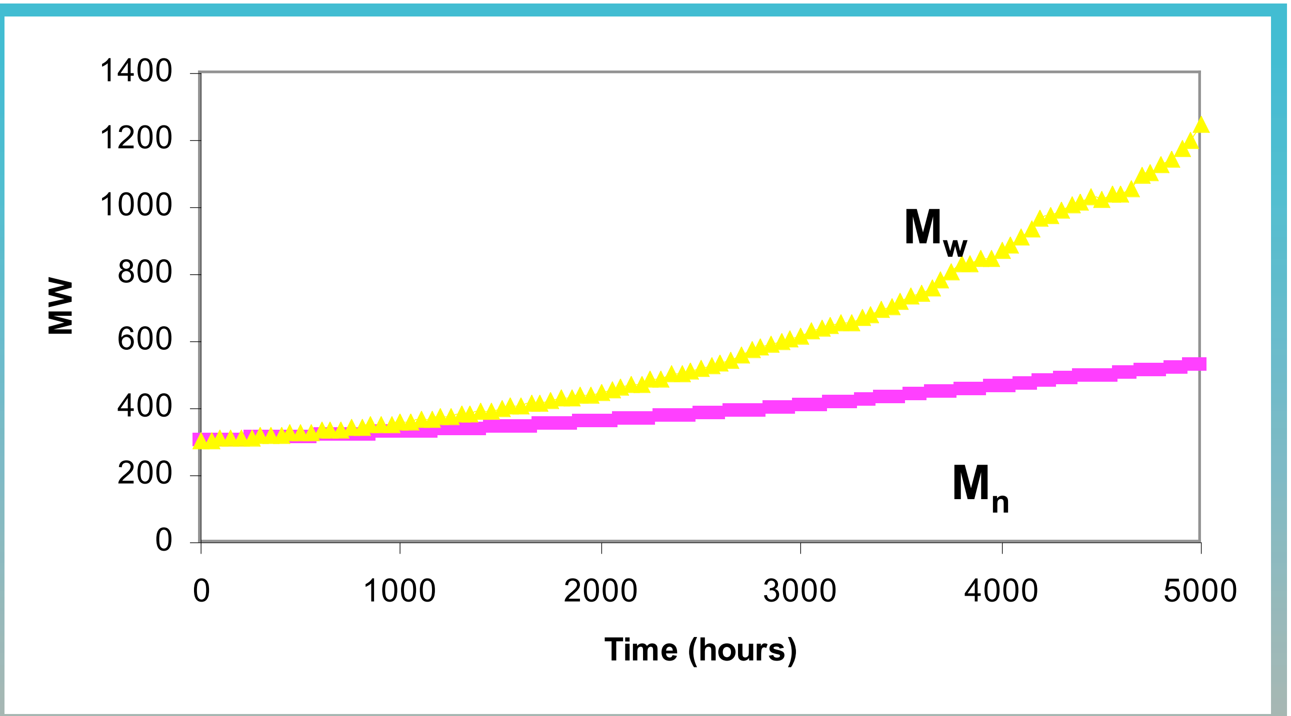
Reduced O_2 (0.1 mM) — Acidic pH (4.0)

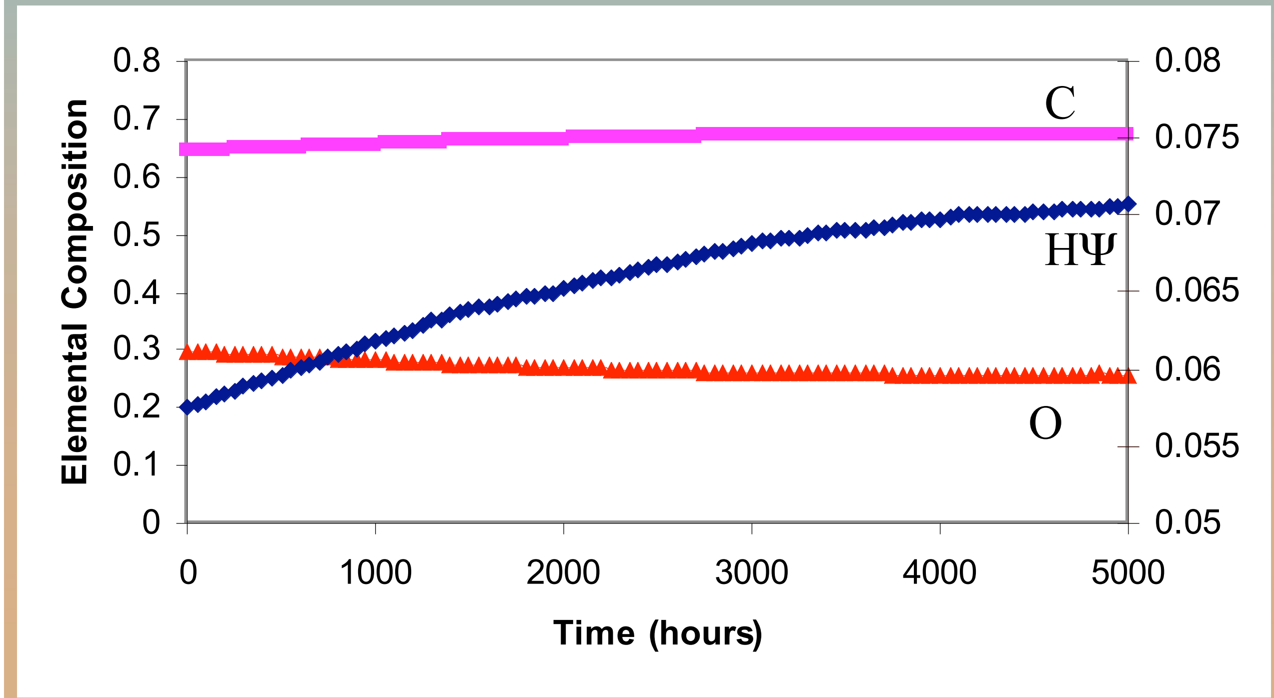
Low oxidase activity (0.03) — ~5.5 months

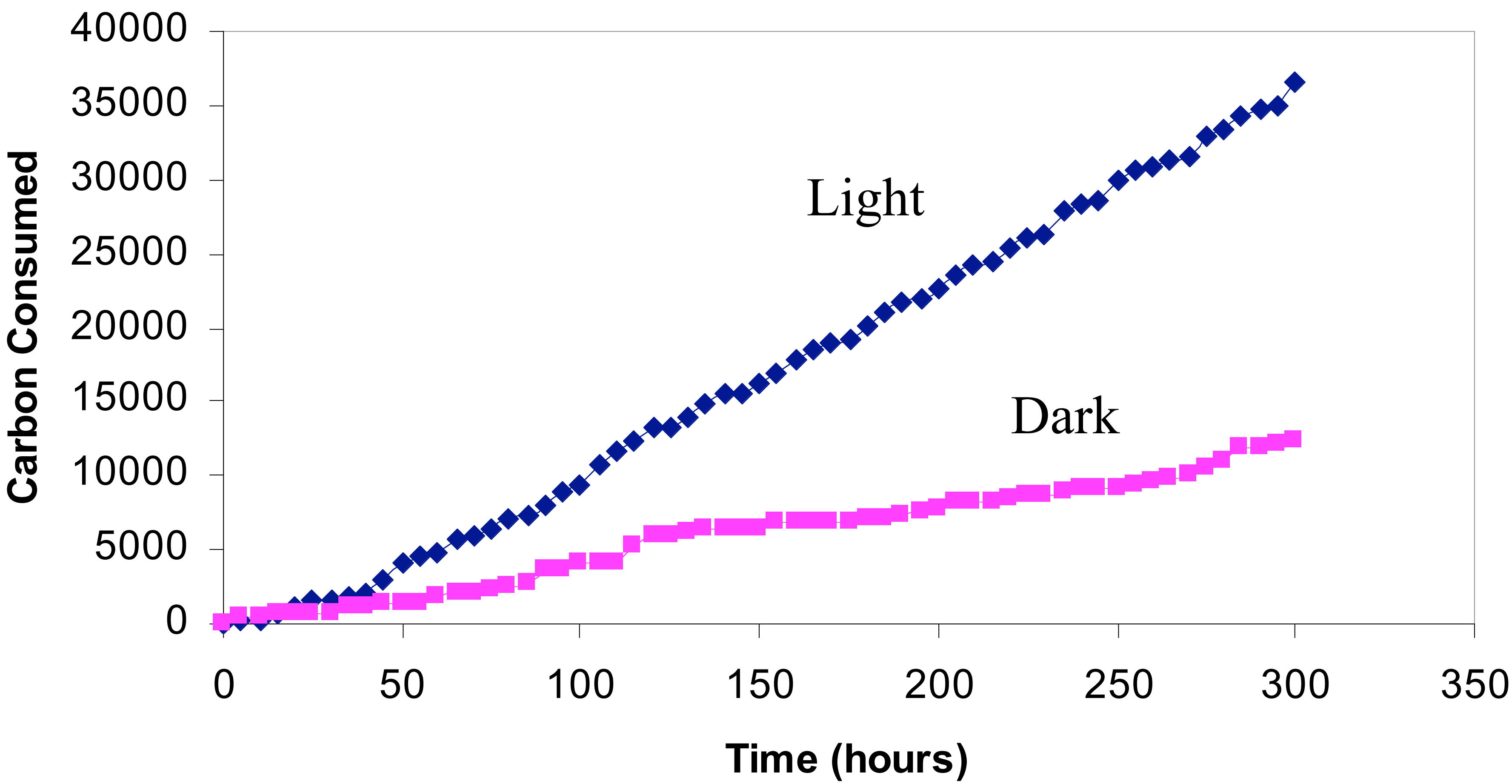
Bacterial density 0.01 — dark

Evolution of NOM from small natural products in low-O_2 soil

Final M_n = 528 amu,
M_w = 1246 amu
67% C, 26% O, and 7 %H







Bacterial carbon consumption is roughly 3X higher in the light simulation than in the dark, with the ratio increasing over time.

Agent-based stochastic synthesis

Produces heterogeneous mixtures of 'legal' molecular structures by condensation and lysis pathways

Bulk composition (elemental %, acidity, aromaticity, MW) similar to NOM

Distributions of MW, pK_a, K_{Cu} consistent with experiment

Plausible ecological results

Next Steps-

- Property prediction algorithms
  - Light absorption
  - IR, nmr, mass spectra
- Spatial and temporal controls
  - Diurnal and seasonal changes
  - Spatial modeling of soils, streams
- Data mining capabilities

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Collaborating Scientists

Steve Cabaniss (UNM)

Jerry Leenheer (USGS)

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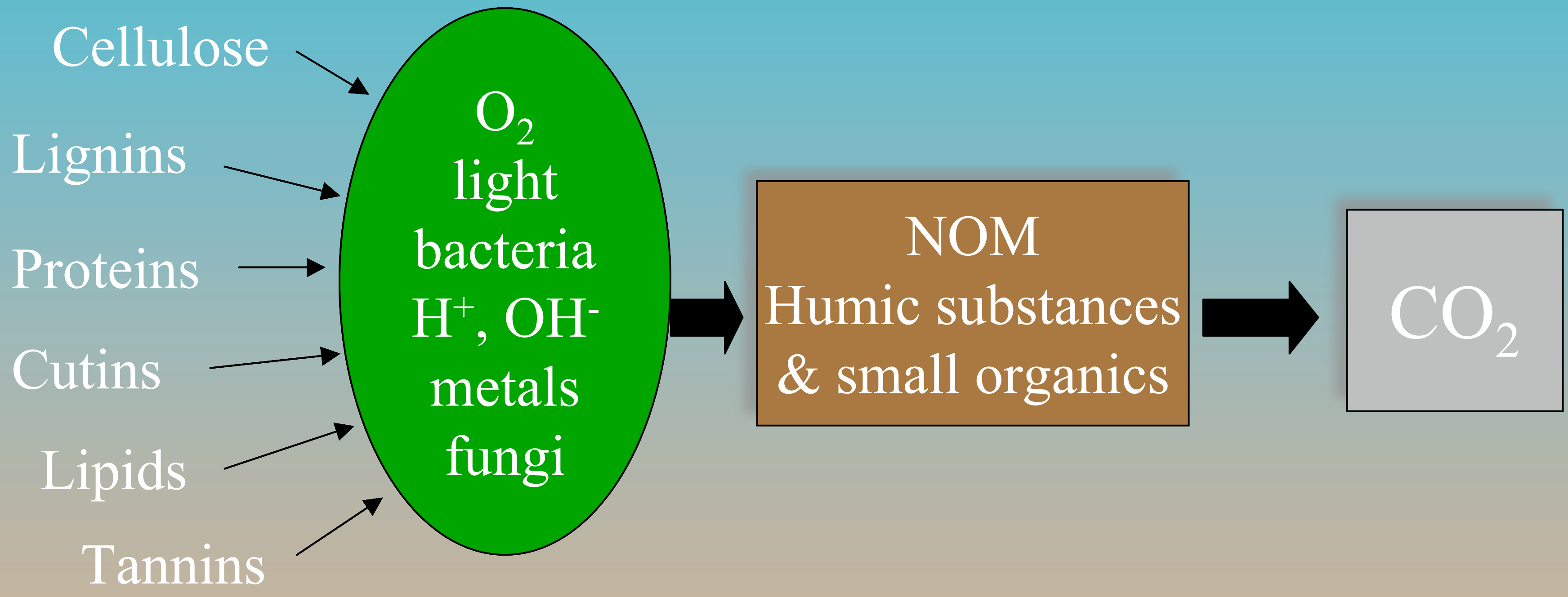
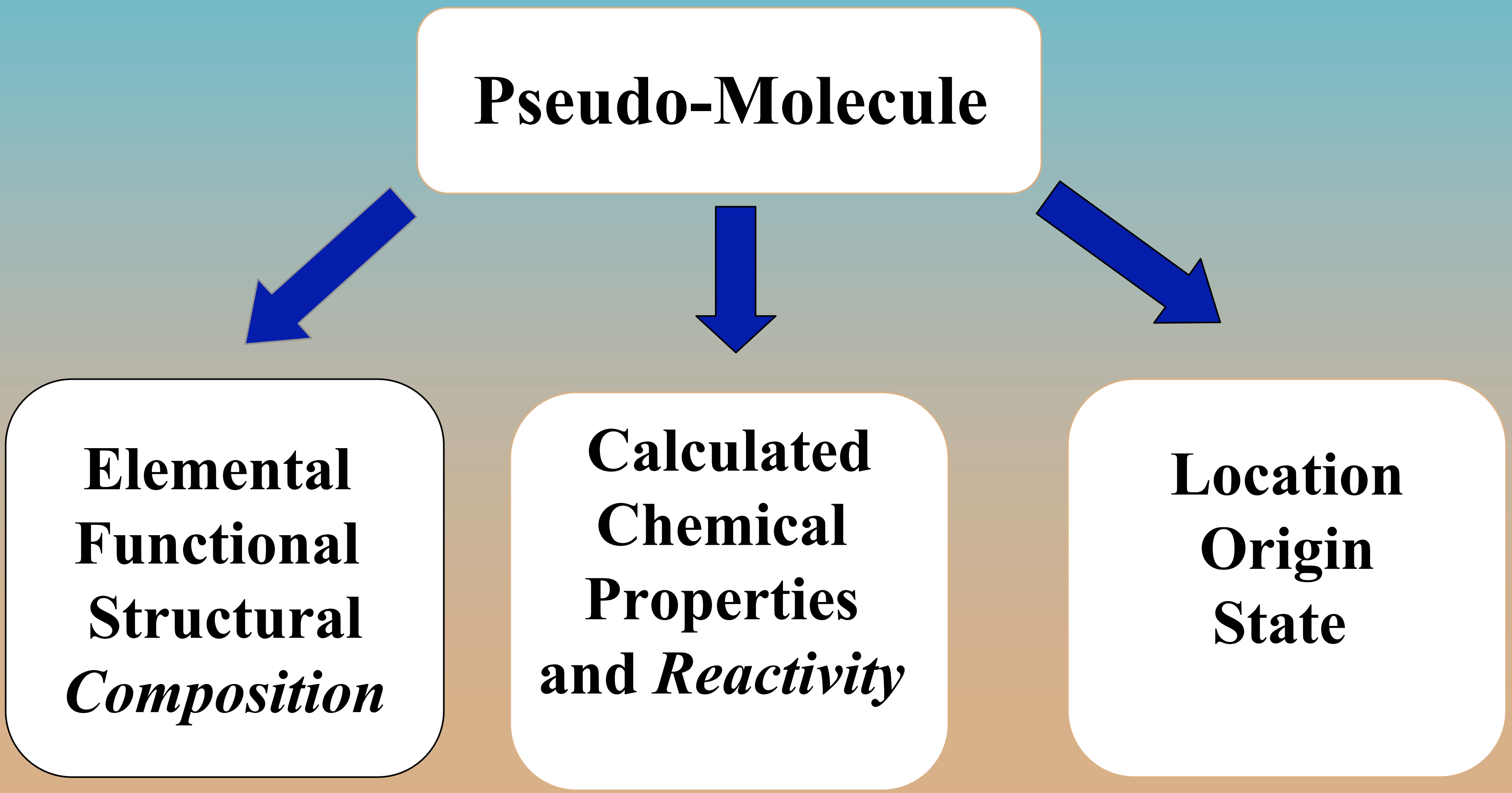
Stochastic Synthesis of NOM



Goal: A widely available, testable, mechanistic model of NOM evolution in the environment.

Stochastic synthesis: Data model



Stochastic synthesis: Environmental Parameters

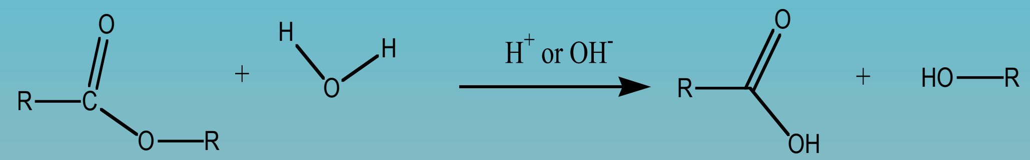
Physical:
Temperature
Light Intensity

Chemical:
Water
pH
[O_2]

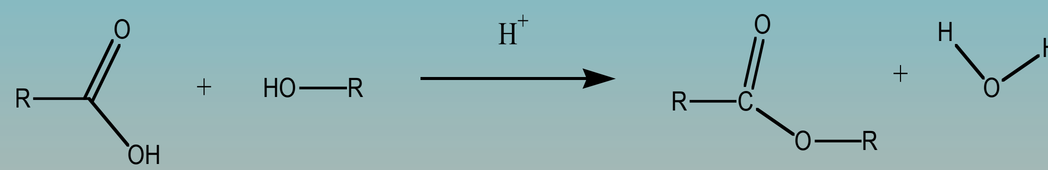
Biological:
Bacterial Density
Oxidase Activity
Protease Activity
Decarboxylase Activity

Model reactions transform structure

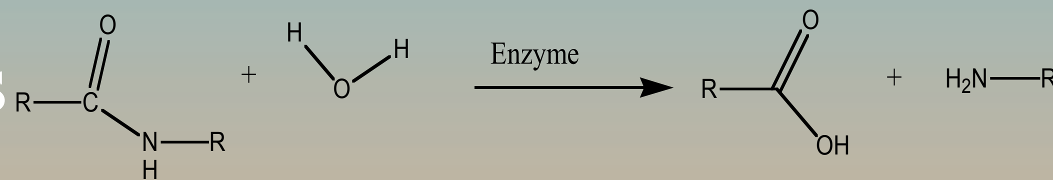
Ester Hydrolysis



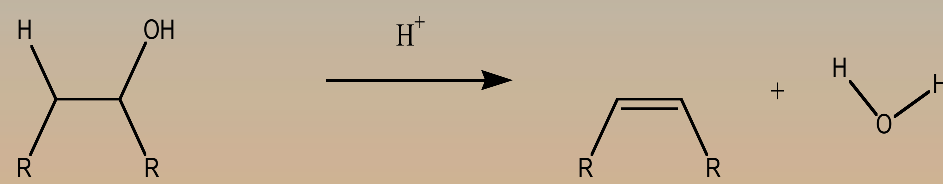
Ester Condensation



Amide Hydrolysis



Dehydration



Microbial uptake