Stochastic Synthesis of Natural Organic Matter

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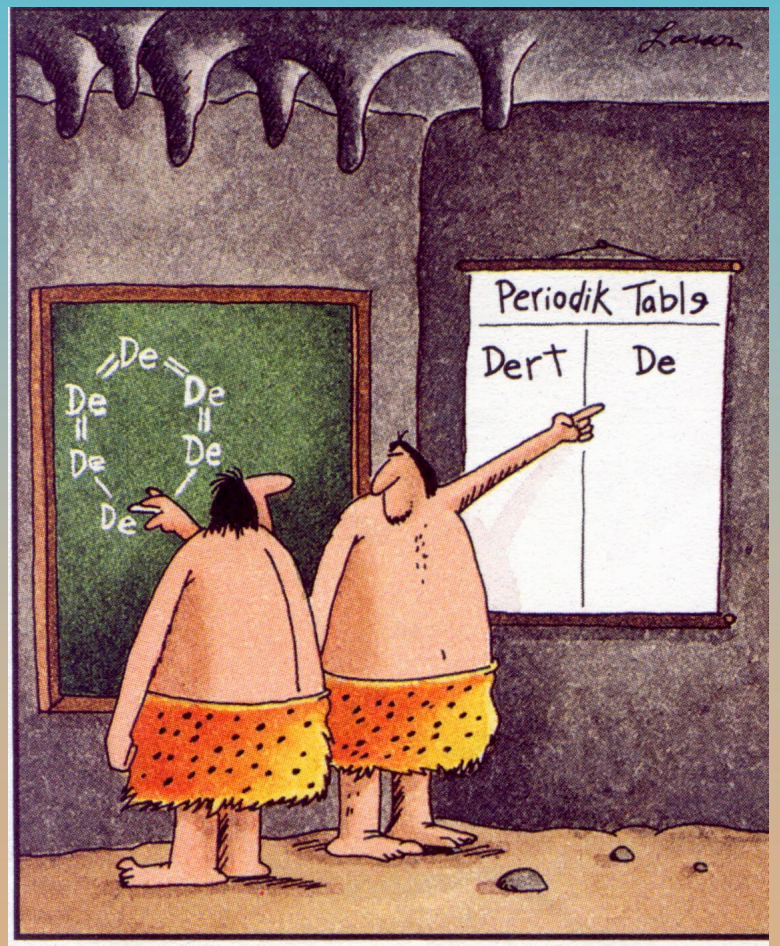
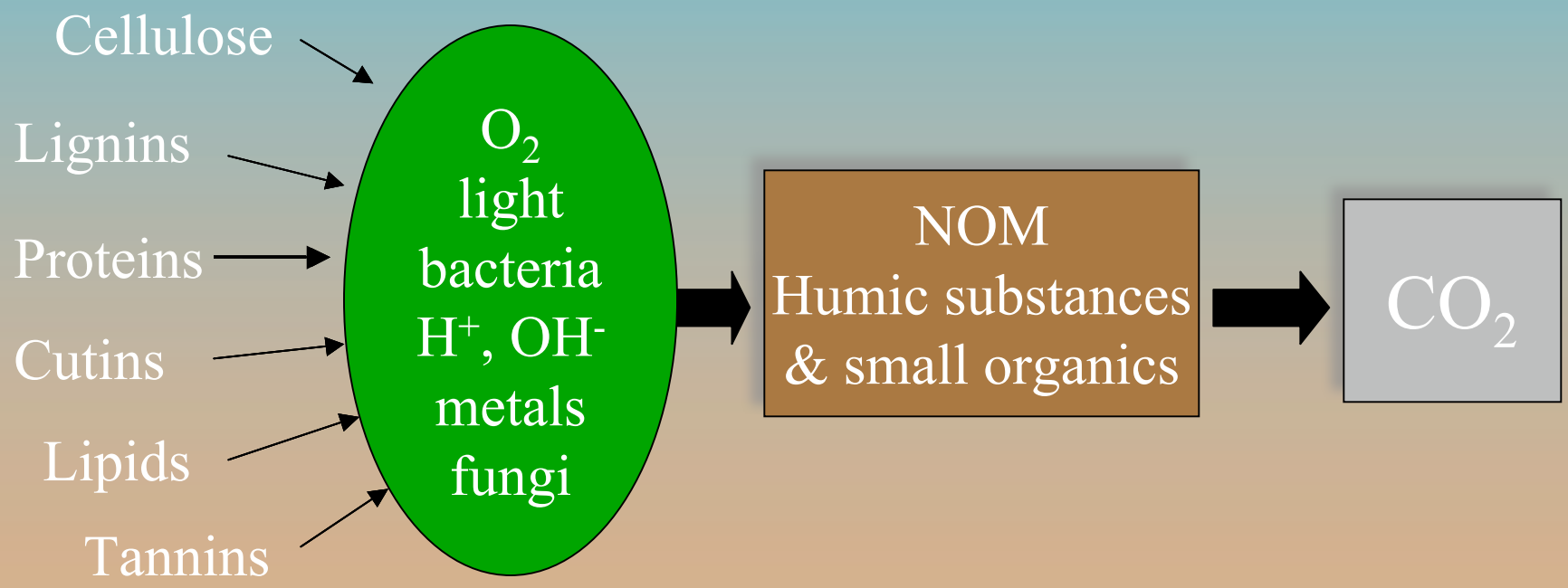
NOM Questions:

- How is NOM produced & transformed in the environment?
- What is its structure and reactivity?



Early chemists describe the first dirt molecule.

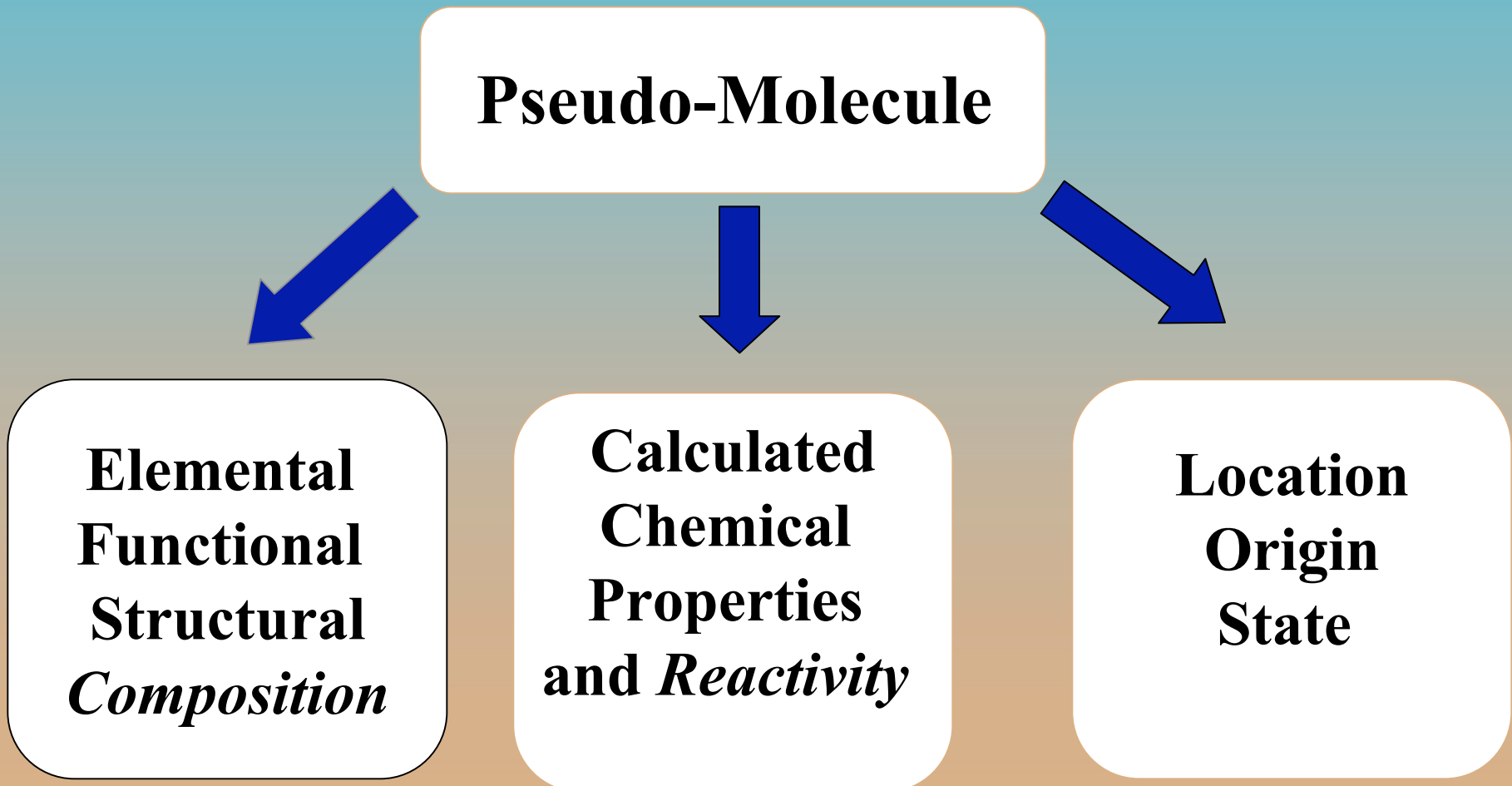
Environmental Synthesis of Natural Organic Matter



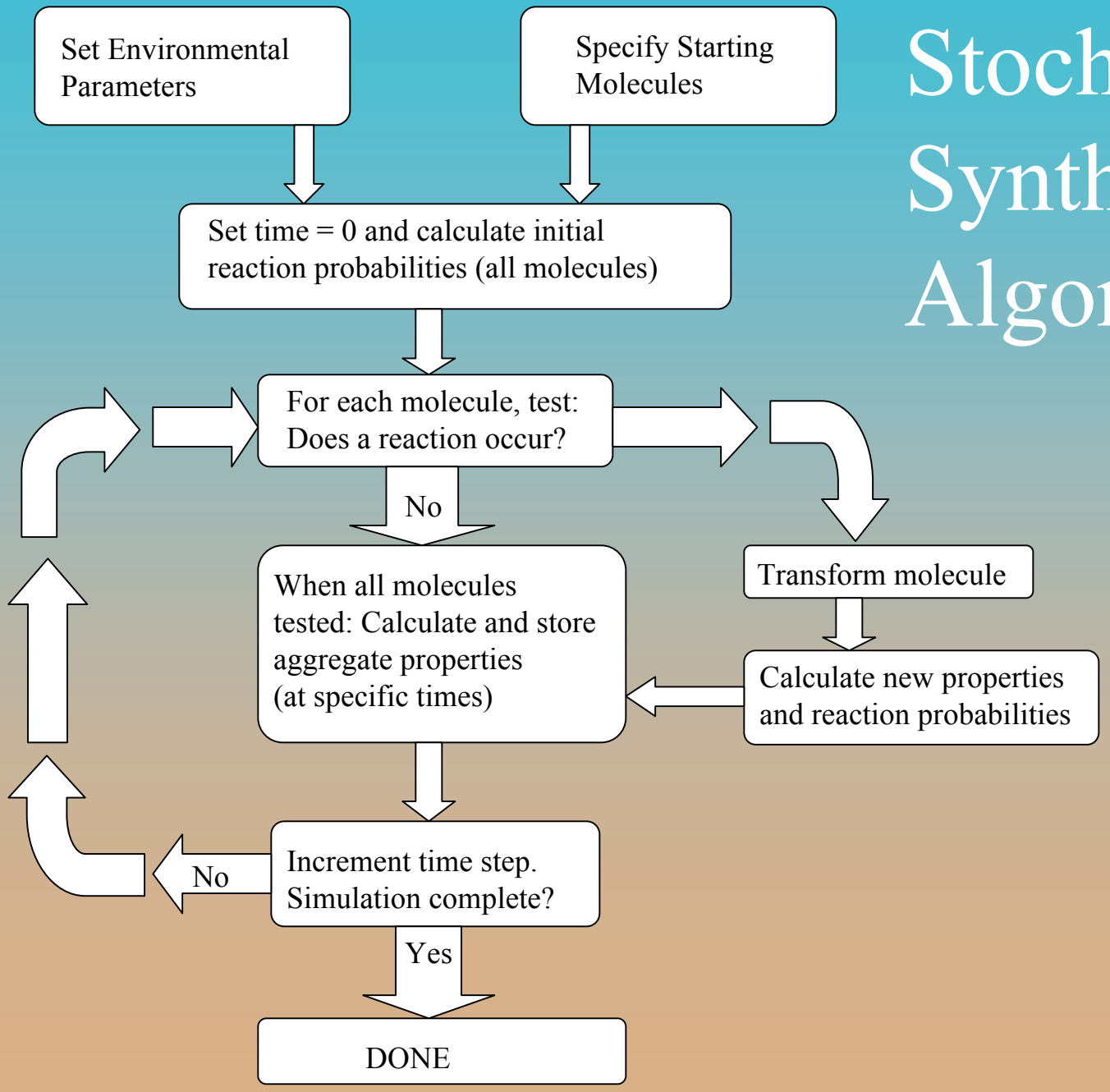
Stochastic Synthesis with AlphaStep: Forward modeling of NOM Evolution

- Agent-based stochastic model using individual molecules- 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

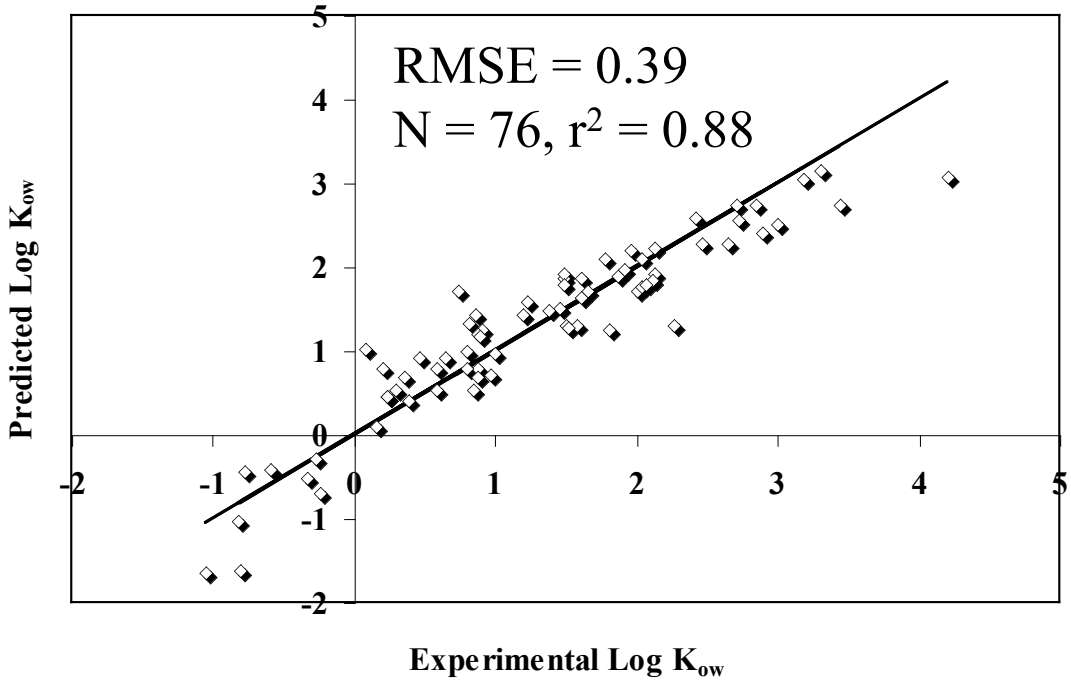
Stochastic synthesis: Data model

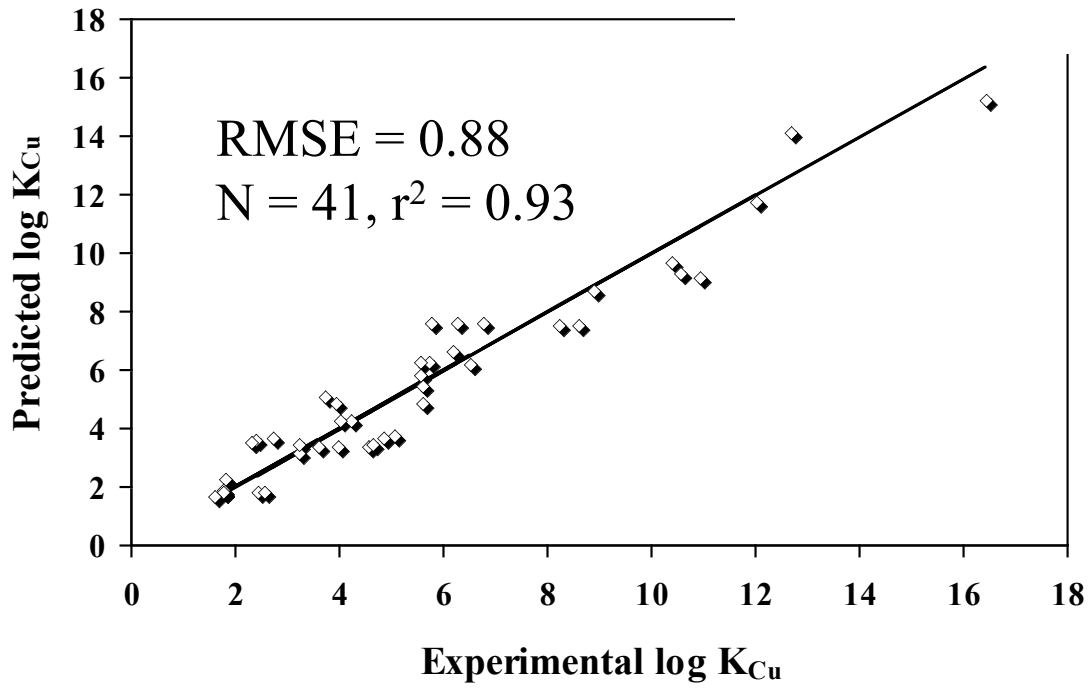


Stochastic Synthesis: Algorithm



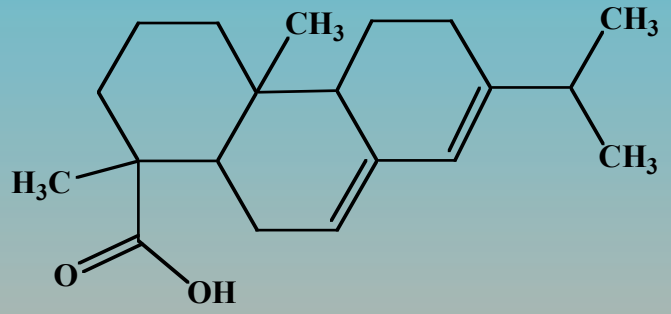
QSAR predictions of K_{Cu}, K_{ow}



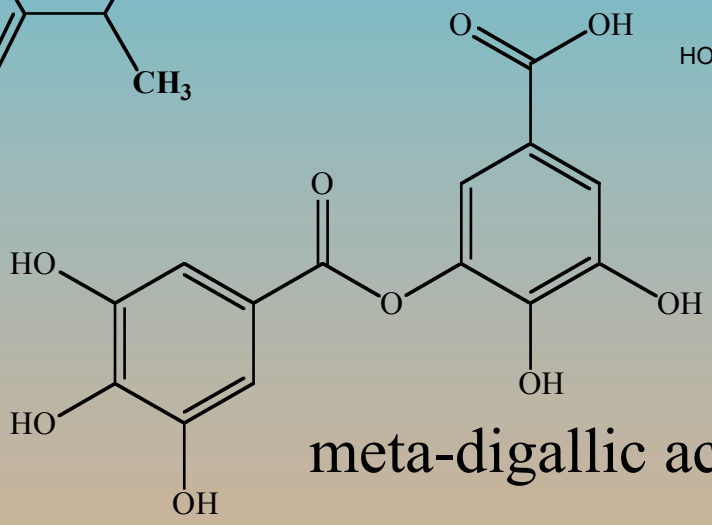


Using only elemental composition and functional group counts

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

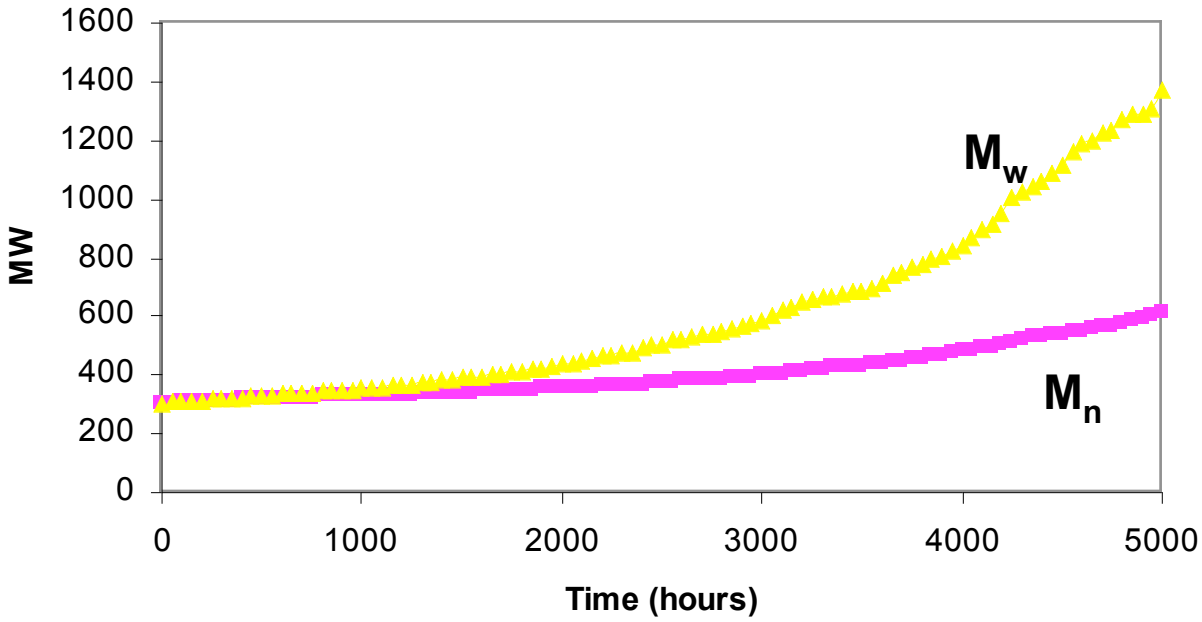
Bacterial density 0.01 dark

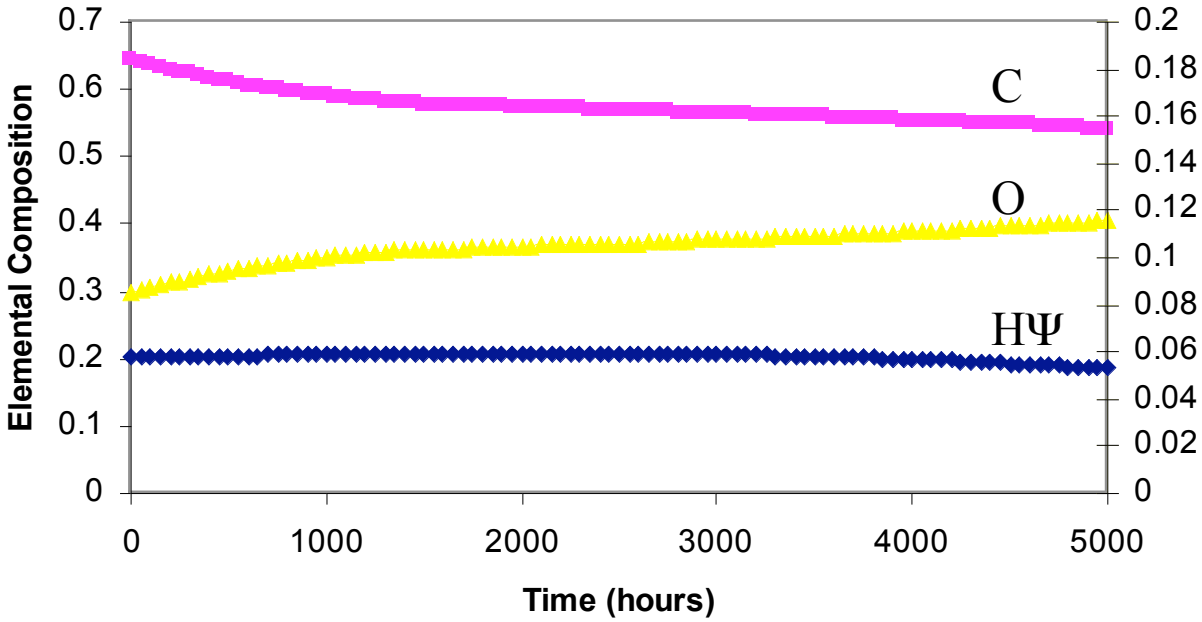
Evolution of NOM from small natural products in oxic soil

Final M_n = 612 amu,

M_w = 1374 amu

54% C, 5% H, 41%O



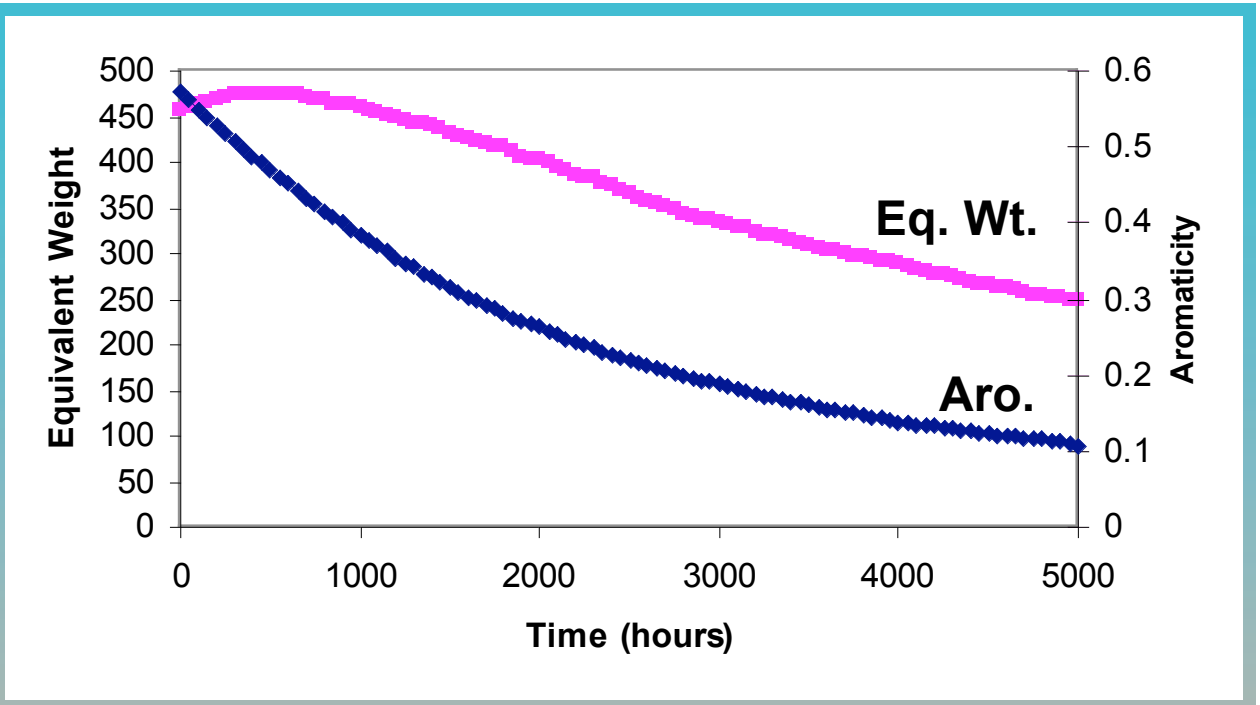


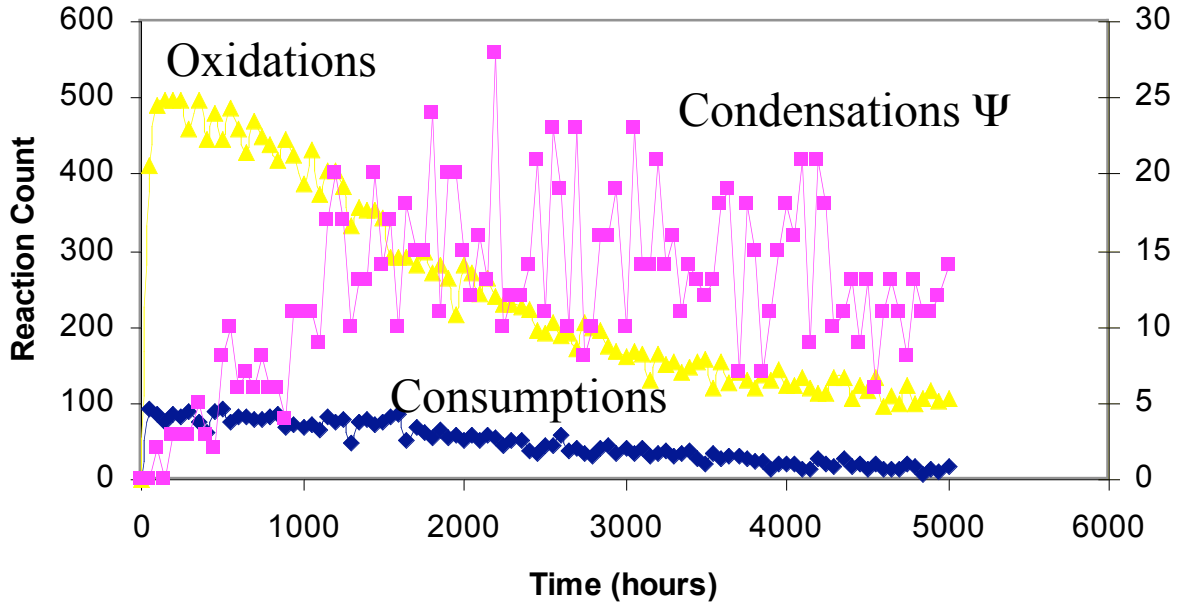
Evolution of NOM from small natural products in oxic soil

Final

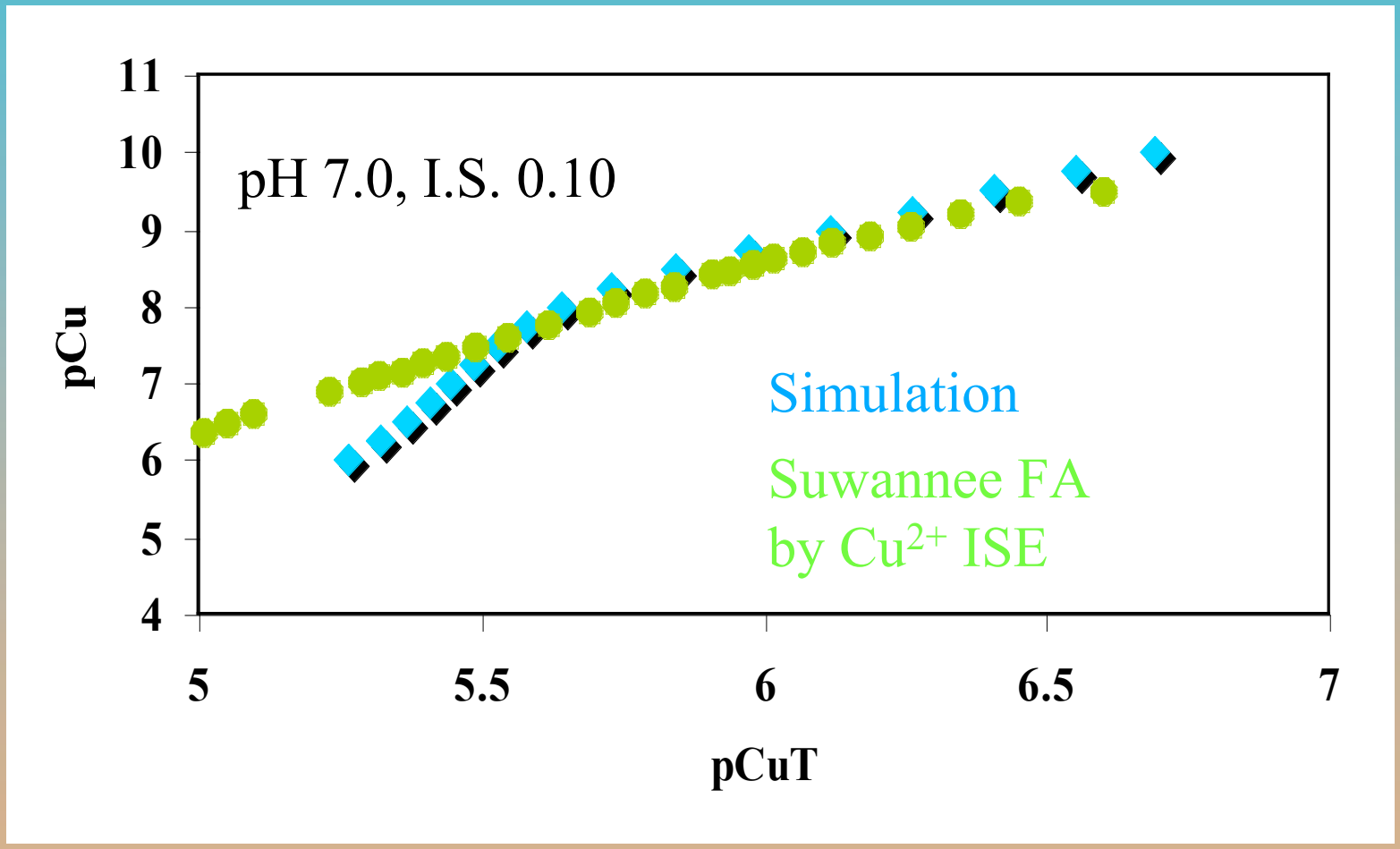
Eq. Wt. = 247 amu,

Aromatic C 11%



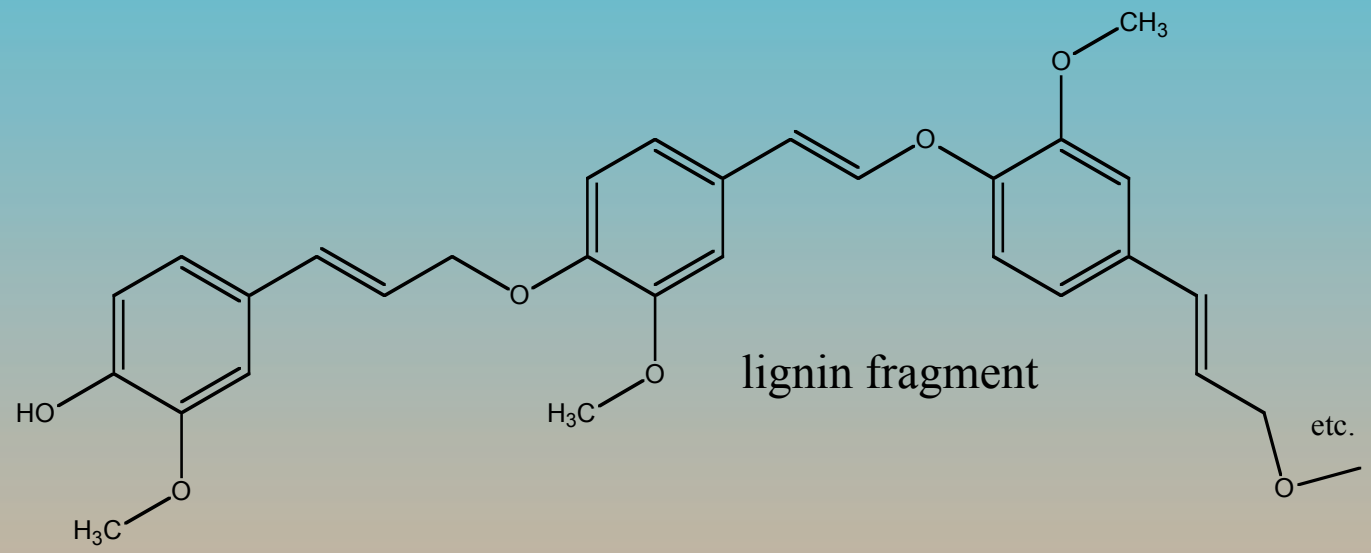


Predicting Cu(II) Complexation



Soil assemblage assuming 1:1 binding to all molecules, K_{Cu} by QSAR

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



lignin fragment

Atmospheric O_2 (0.3 mM)

Neutral pH (7.0)

Lower enzyme activity (0.01)

4 months reaction time

Medium light ($2x10^{-8}$ mol cm^{-2} hr^{-1})

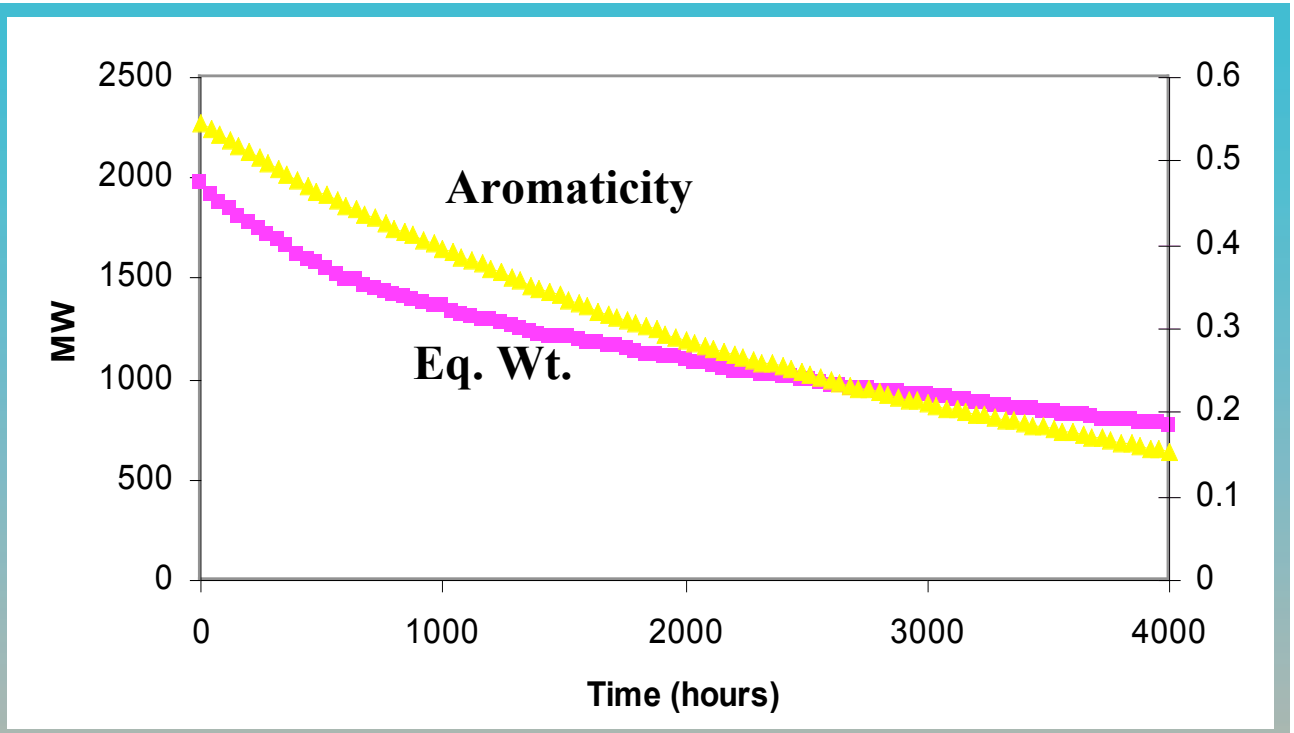
24.8 ^oC

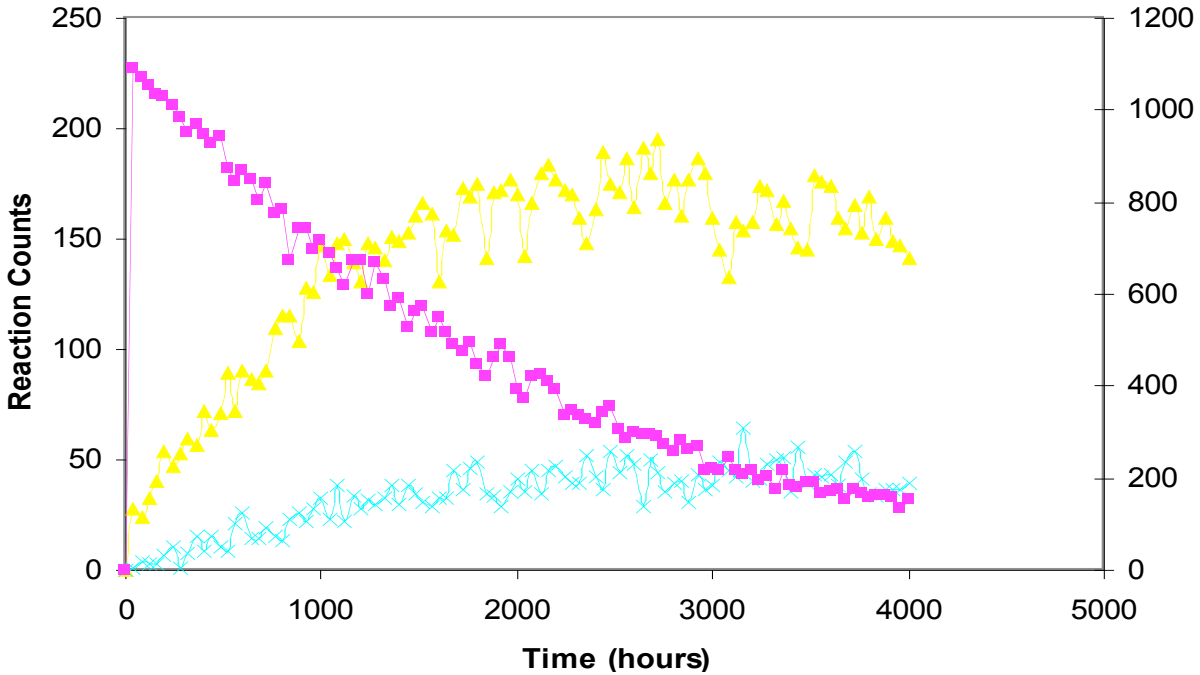
Moderate bacterial density (0.02)

400 molecules lignin and protein

Evolution of NOM from lignin and protein in surface water

Final composition: Eq. Wt. = 772 amu, 15% aromatic C





Evolution of NOM from lignin and protein in surface water

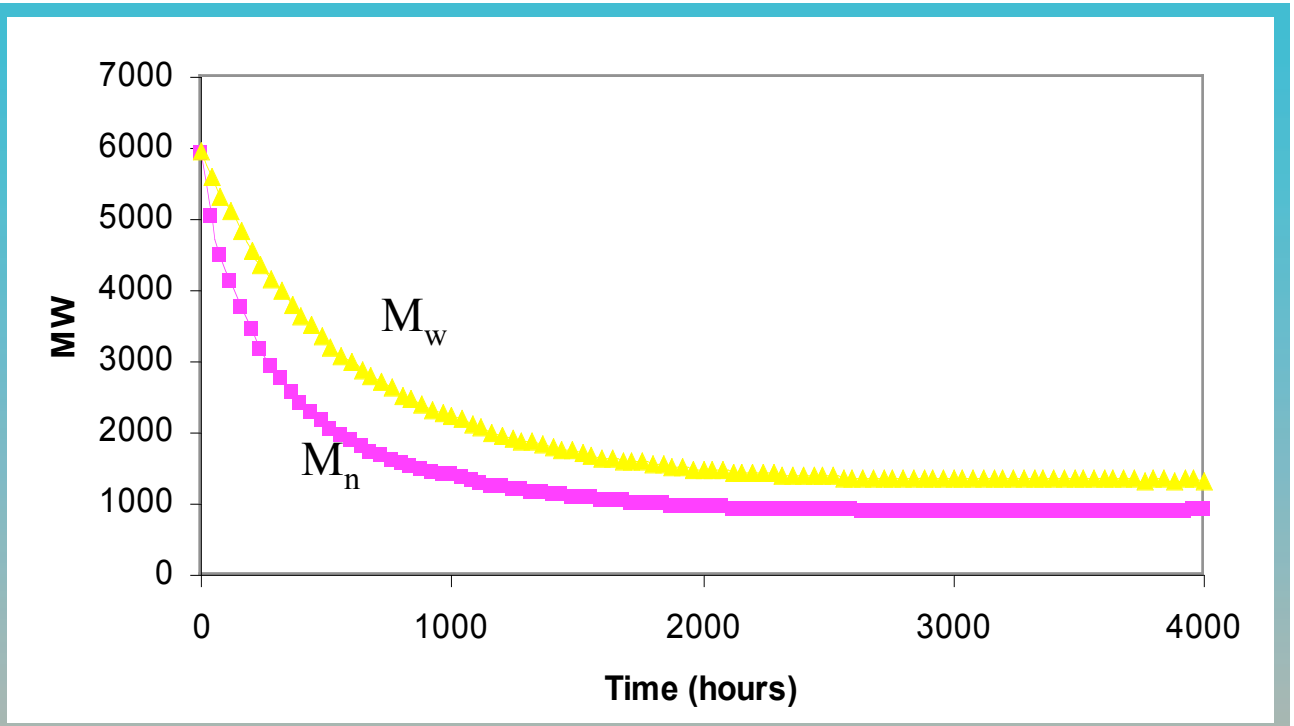
Final M_n = 902 amu,

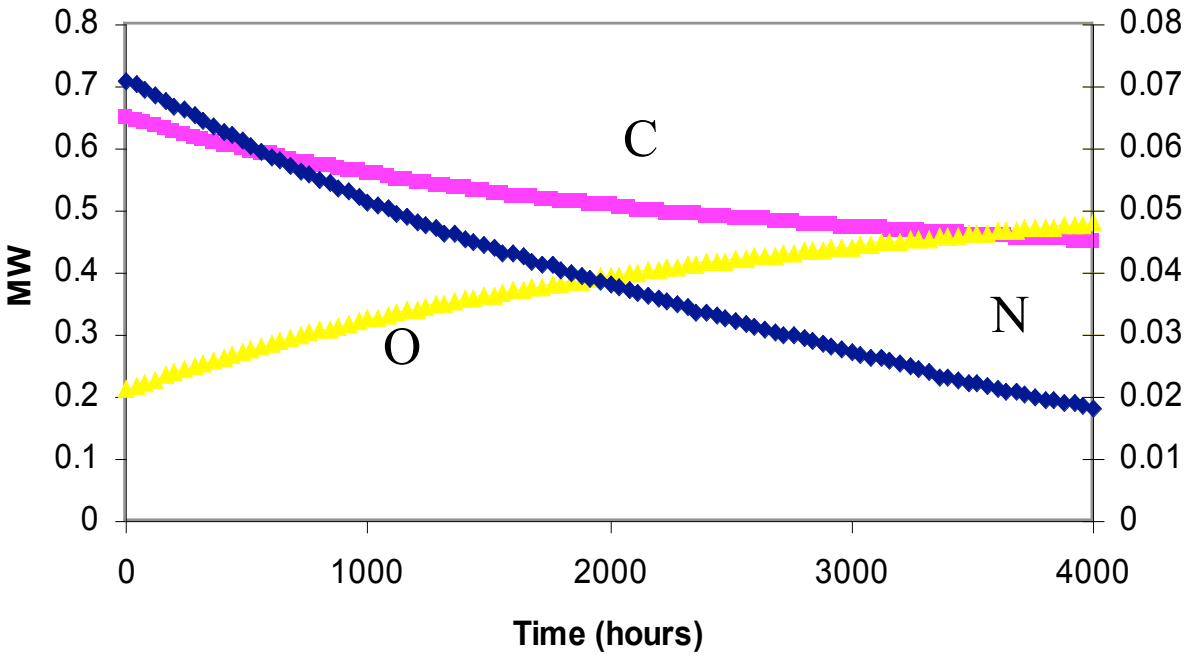
M_w = 1337 amu

(log normal MWD)

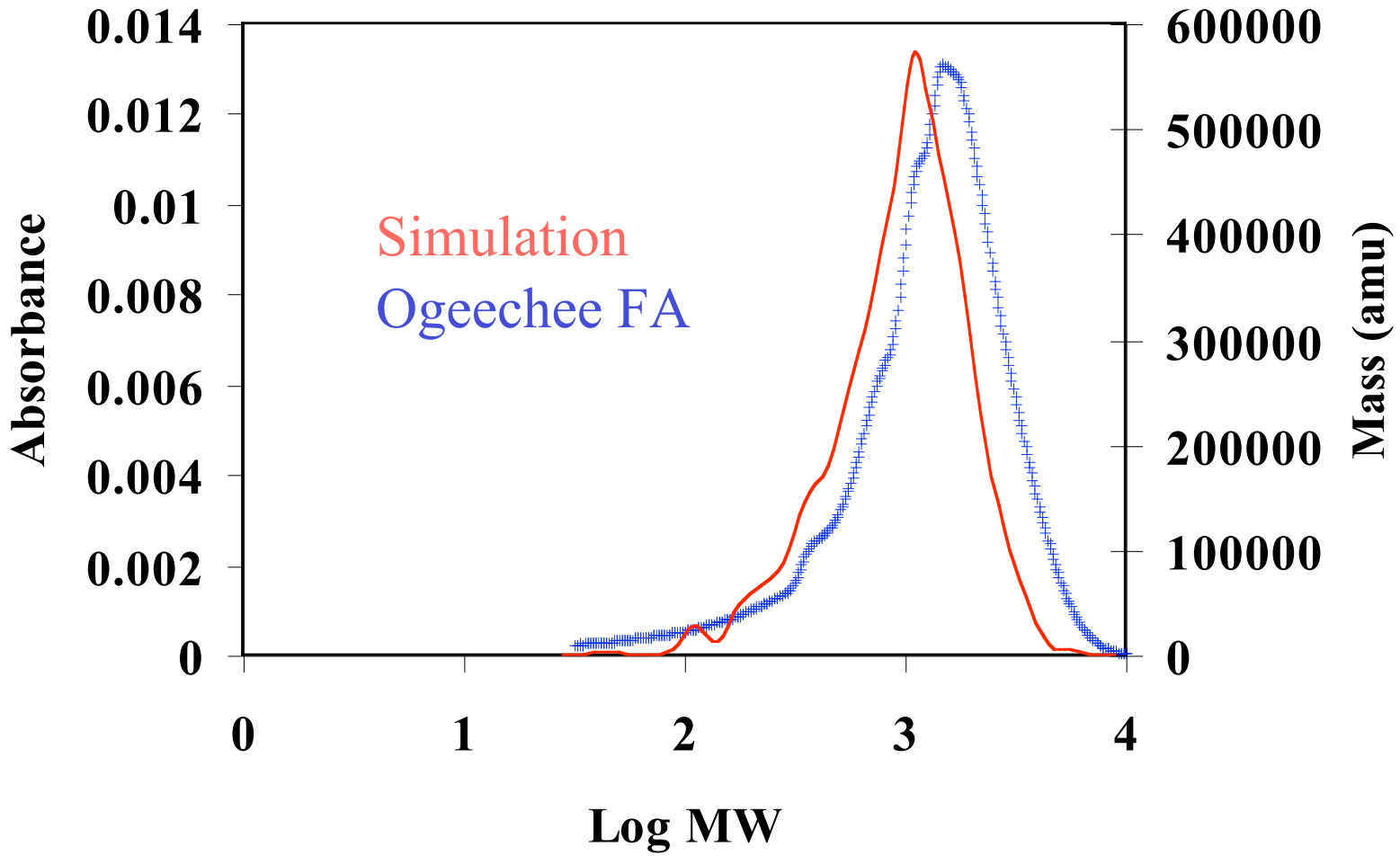
45% C, 48% O,

5.2% H, 1.8% N





MW Distribution: Comparison w/ SE-HPLC



Simulated results lie within range of field measurements

Property	Literature* Range	Simulation Results Soil	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).

Stochastic synthesis

>Produces heterogeneous mixtures of ‘legal’ molecular structures

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

>Both condensation and lysis pathways of NOM evolution are viable

Next Steps-

- Property prediction algorithms
  - UV, IR, nmr spectra
- Spatial and temporal controls
  - Diurnal and seasonal changes
  - ‘continuous reactor’
  - Spatial modeling of soils, streams
- Data mining capabilities

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Collaborating Scientists

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