Stochastic Synthesis of Natural Organic Matter

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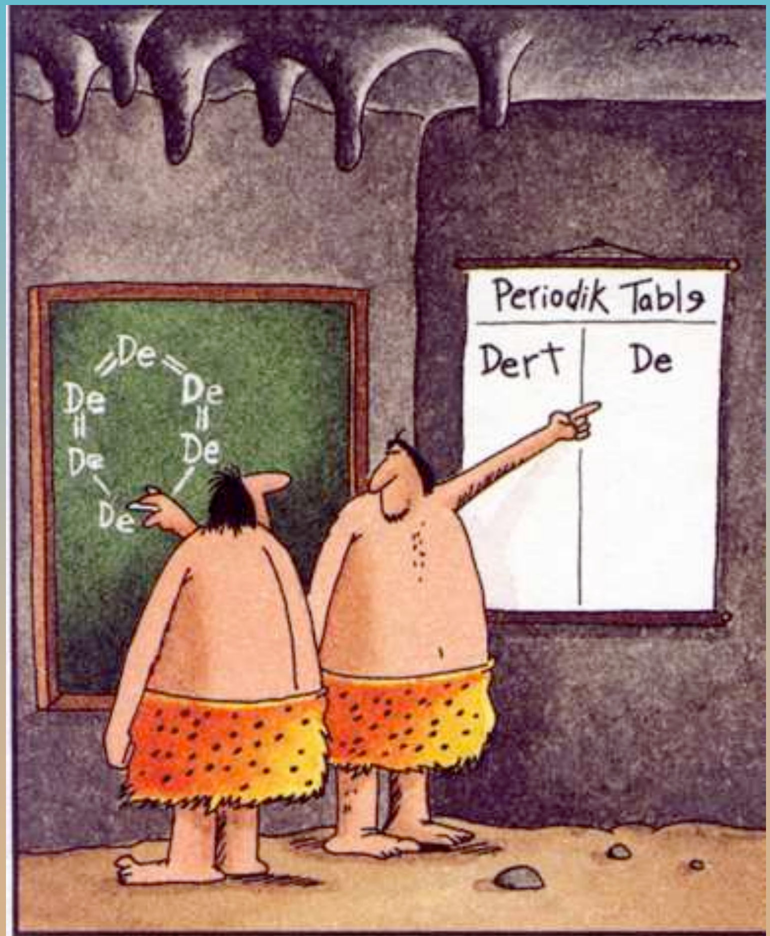
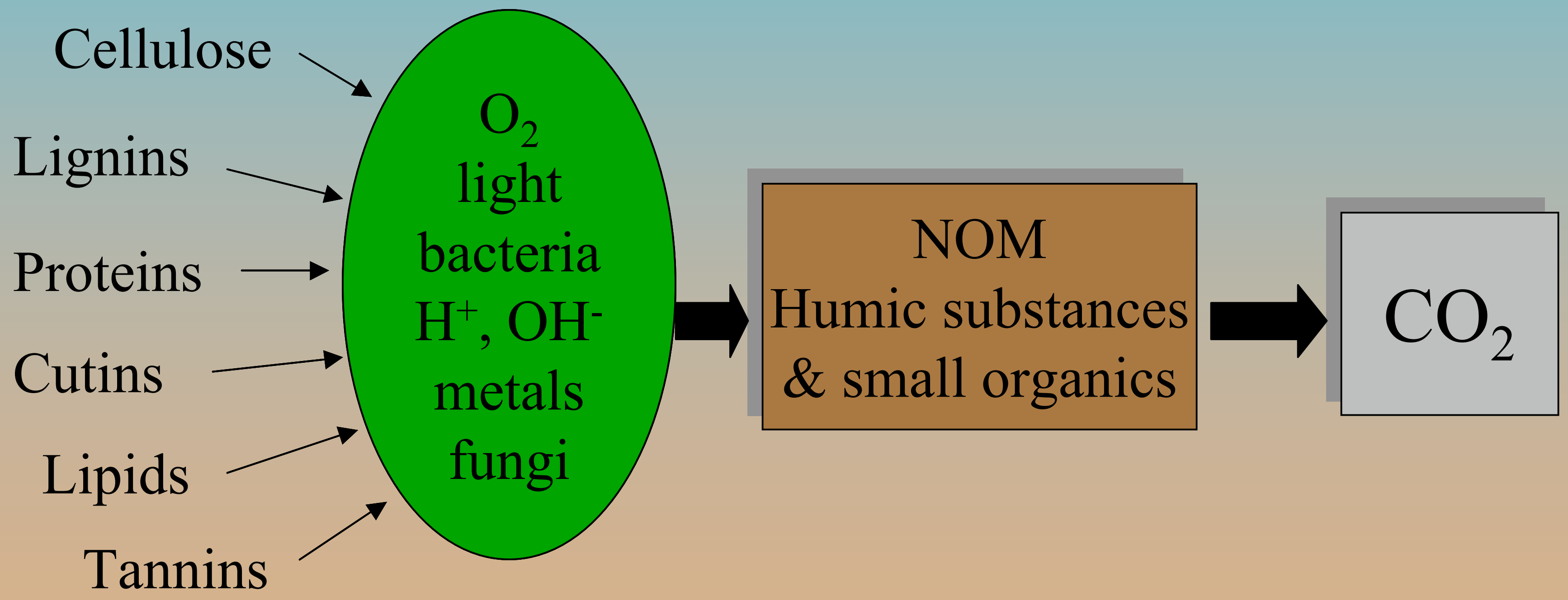
NOM Questions:

- How is NOM produced & transformed in the environment?
- What is its structure and reactivity?
- Can we quantify NOM effects on ecosystems & pollutants?



Early chemists describe the first dirt molecule.

Environmental Synthesis of Natural Organic Matter



Simulating NOM Synthesis
Probabilistic Reaction Kinetics

For first or pseudo-first order reaction

P = k’ _t

P = probability that a molecule will react with a short time interval _t

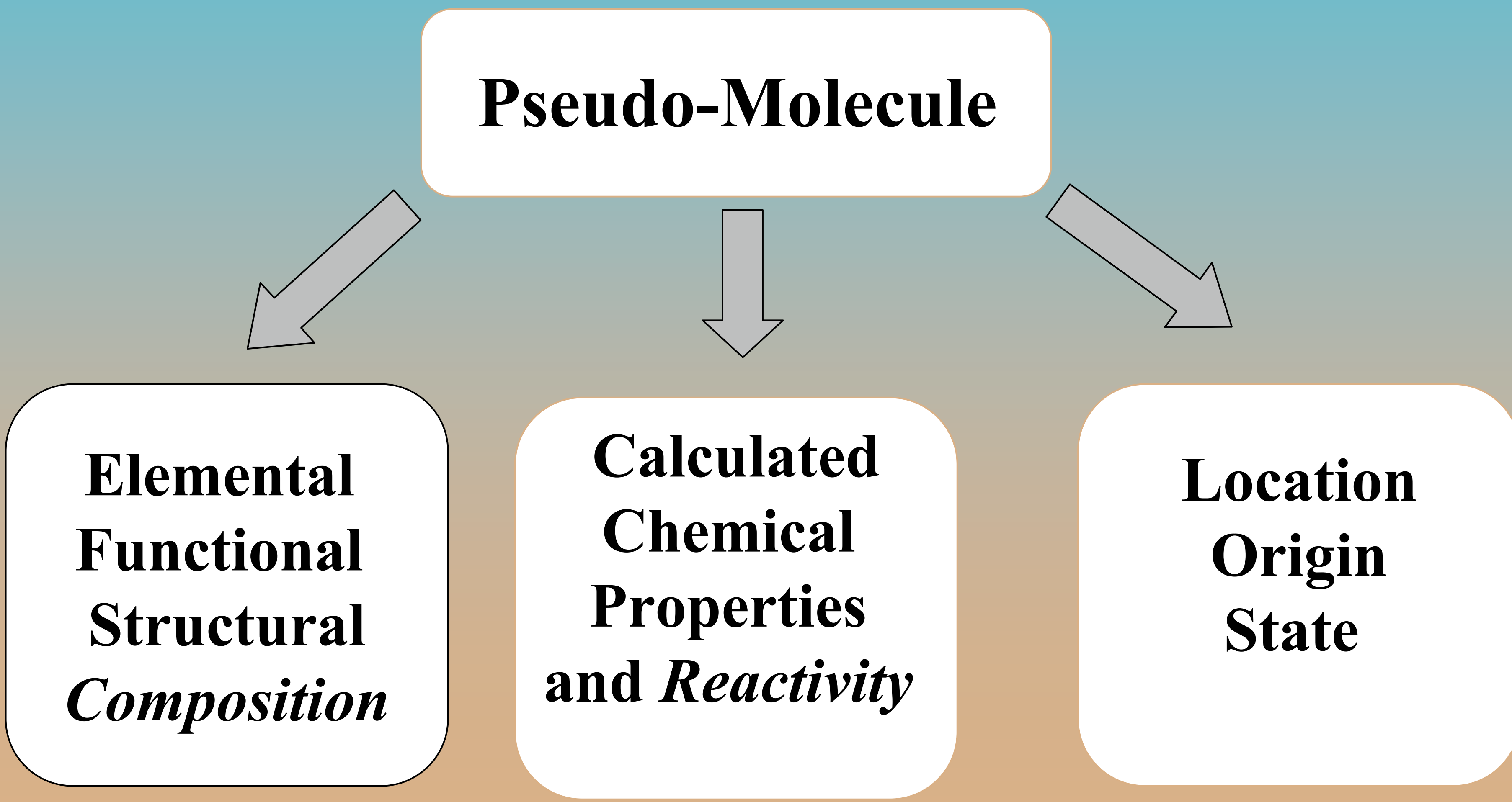
k’ = first or pseudo-first order rate constant units of time^{-1}

Based on individual molecules

Stochastic Algorithm: Advantages

- Computation time increases as # molecules, not # possible molecules
- Flexible integration with transport
- Product structures, properties not pre-determined

Stochastic synthesis: Data model



Stochastic synthesis: Environmental Parameters

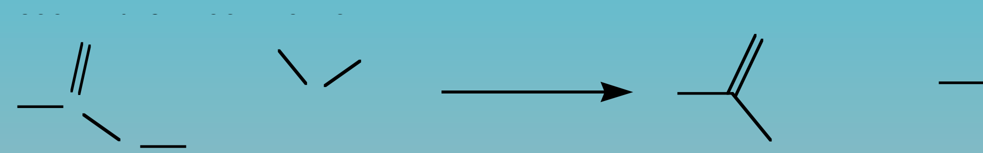
Physical:
Temperature
Light Intensity
Duration

Chemical:
Water
pH
[O_2]

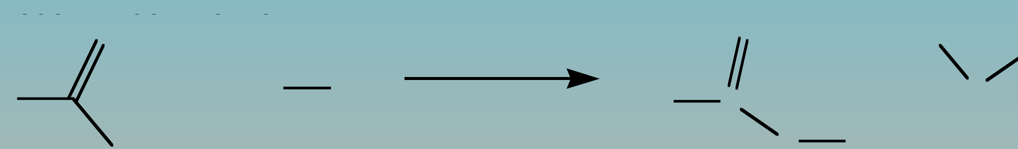
Biological:
Bacterial Density
Oxidase Activity
Protease Activity
Decarboxylase Activity

Model reactions transform structure

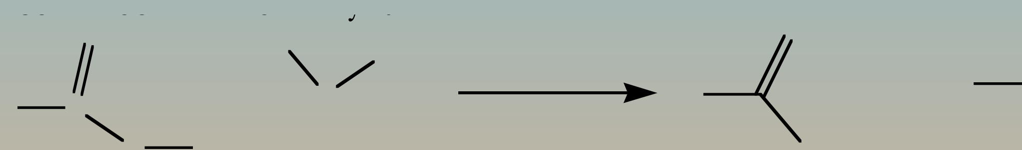
Ester Hydrolysis



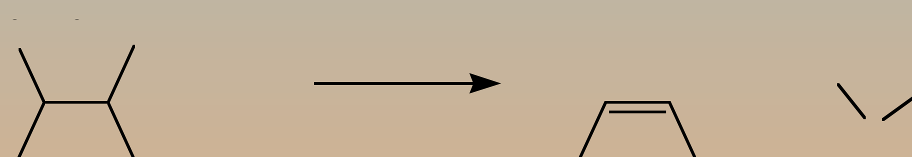
Ester Condensation



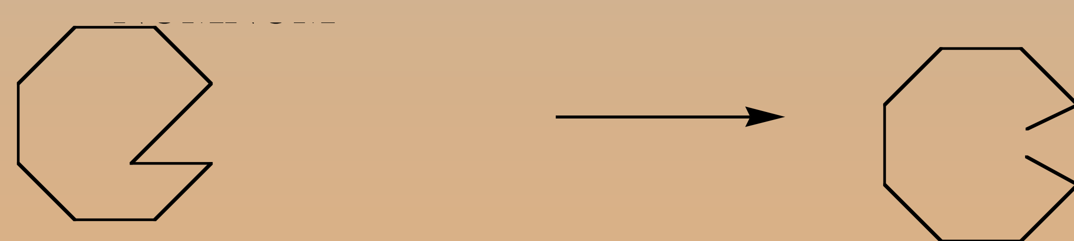
Amide Hydrolysis



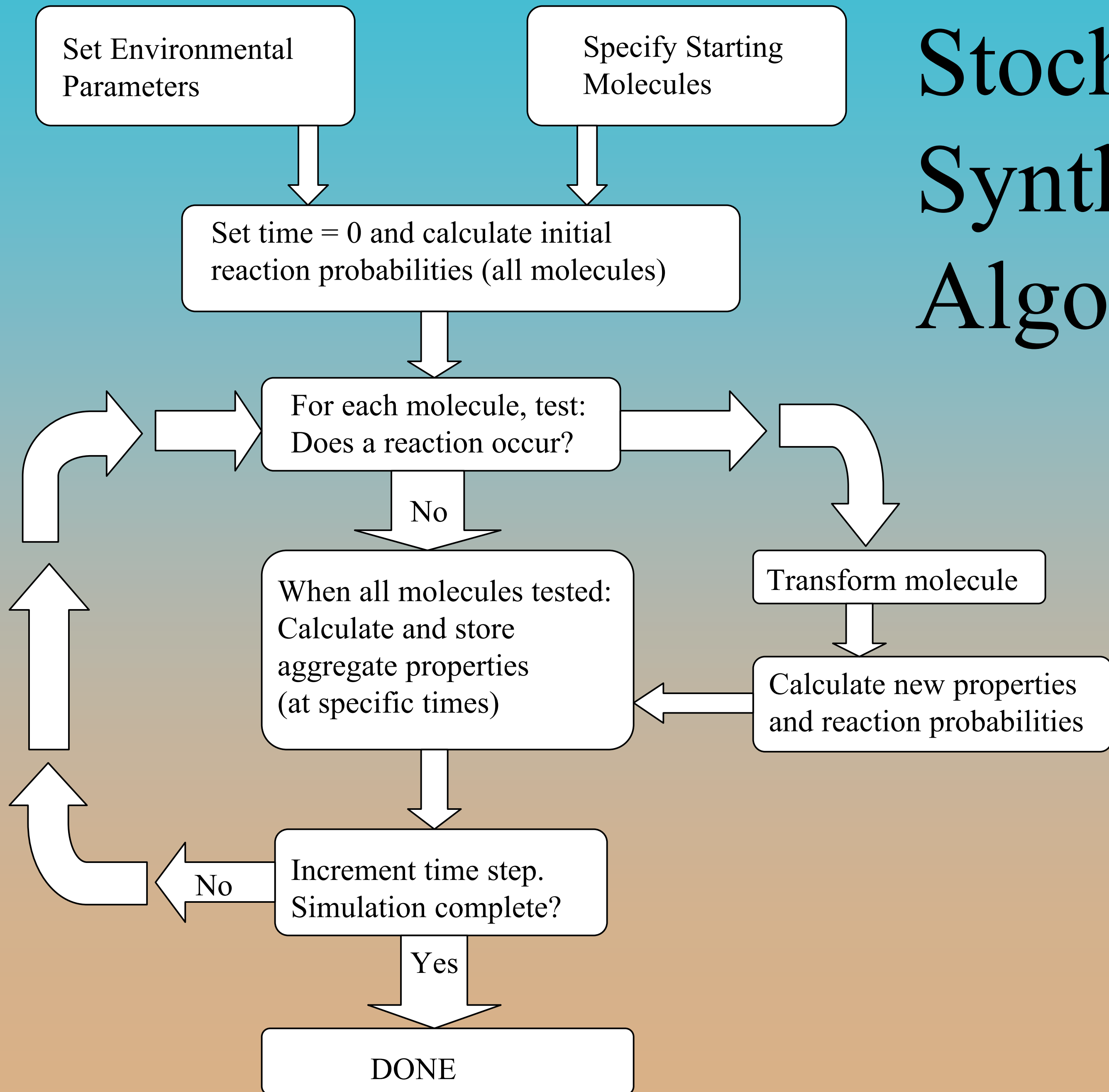
Dehydration



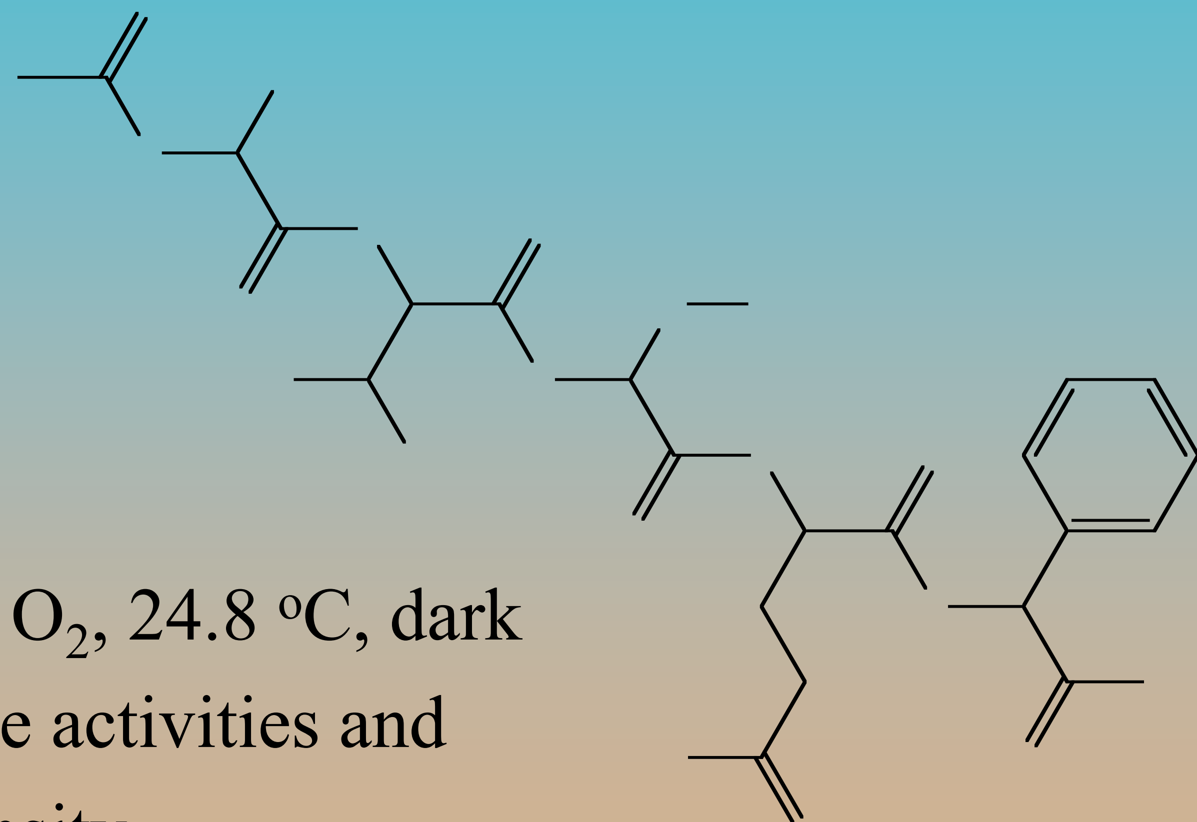
Microbial uptake



Stochastic Synthesis: Algorithm



Hydrolysis and consumption of a protein

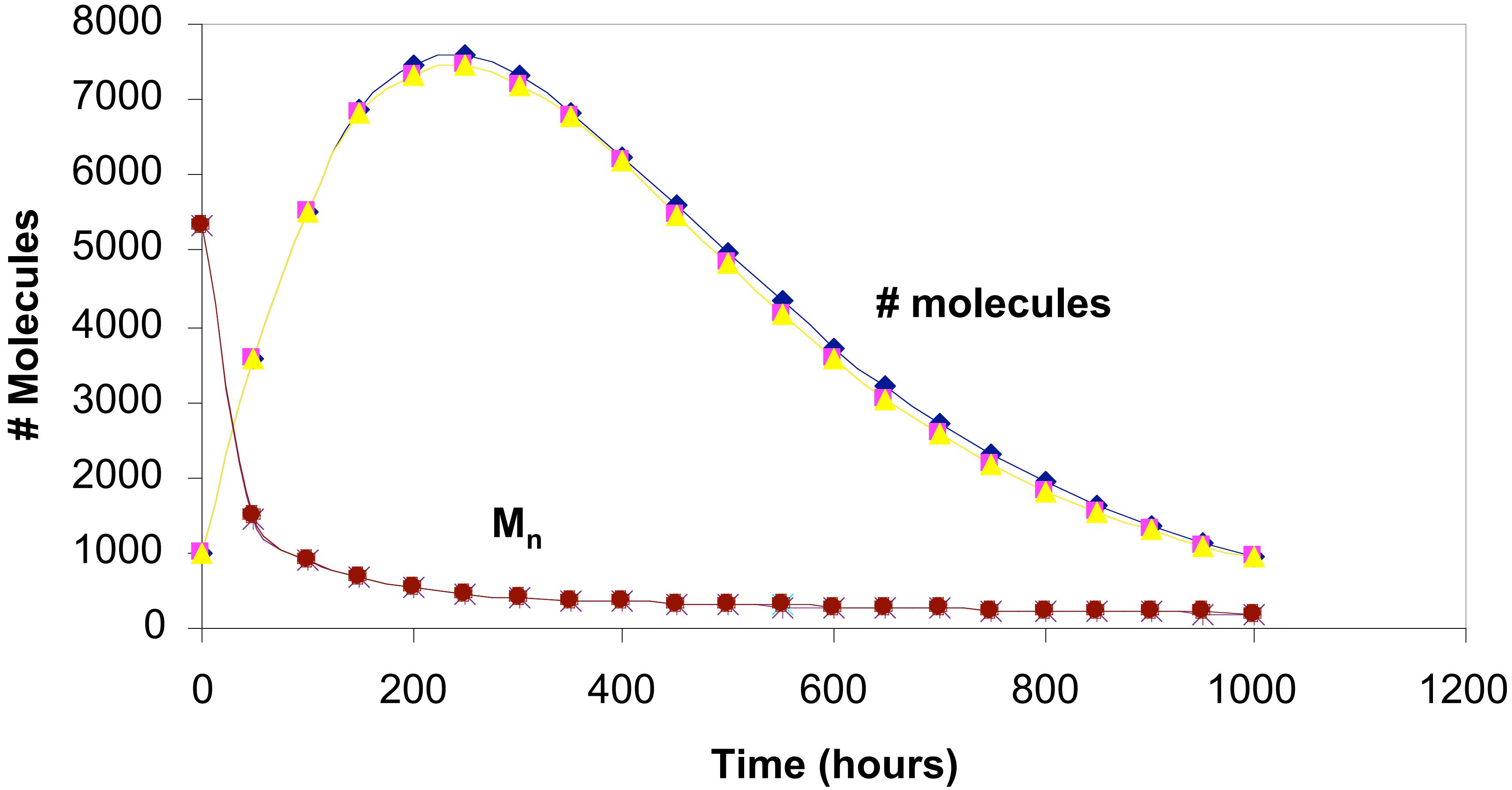


pH 7.0, 0.1 mM O_2, 24.8 ^{o}C, dark

Standard enzyme activities and
bacterial density

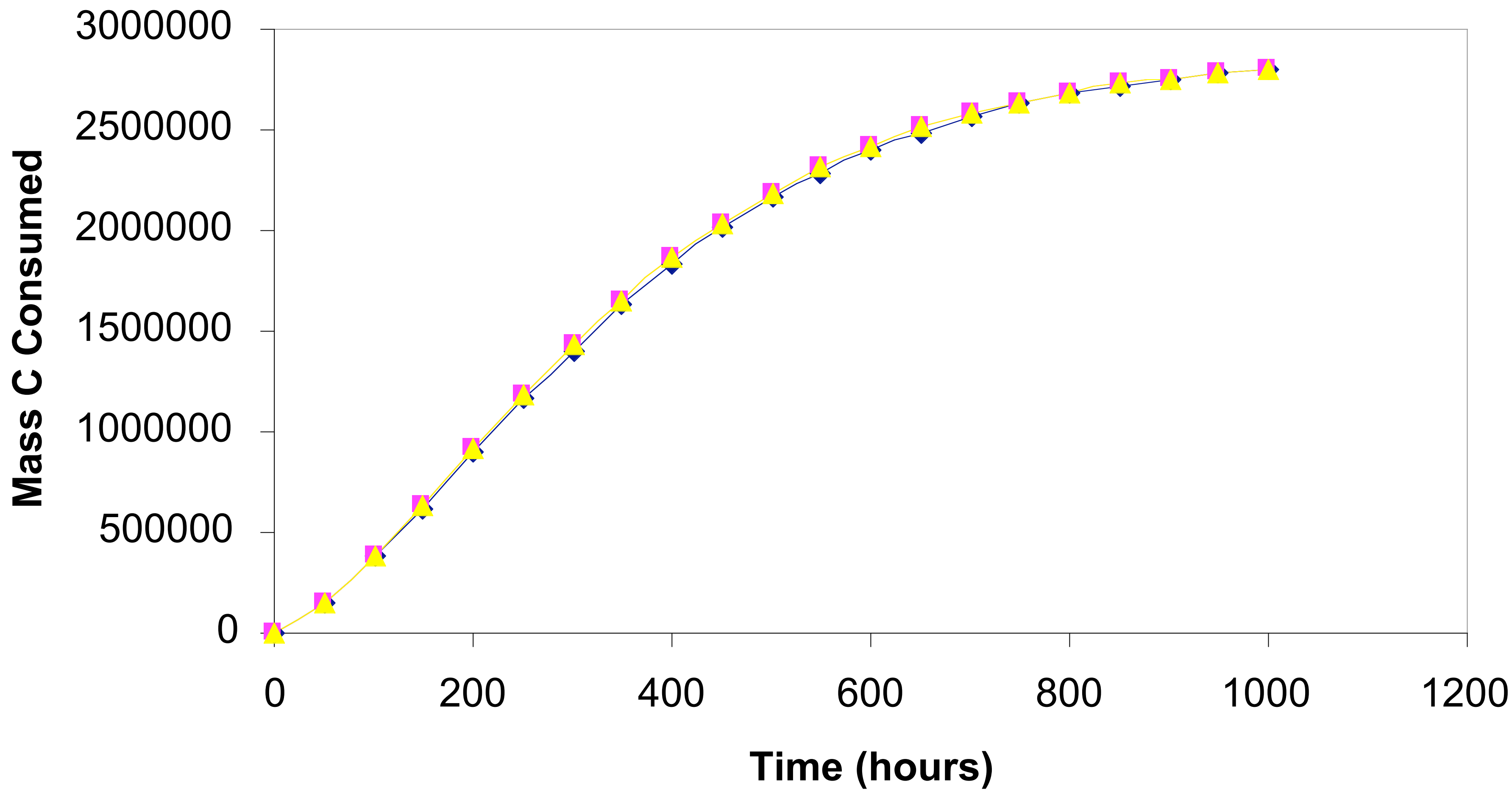
1000 molecules,

1000 hour simulation

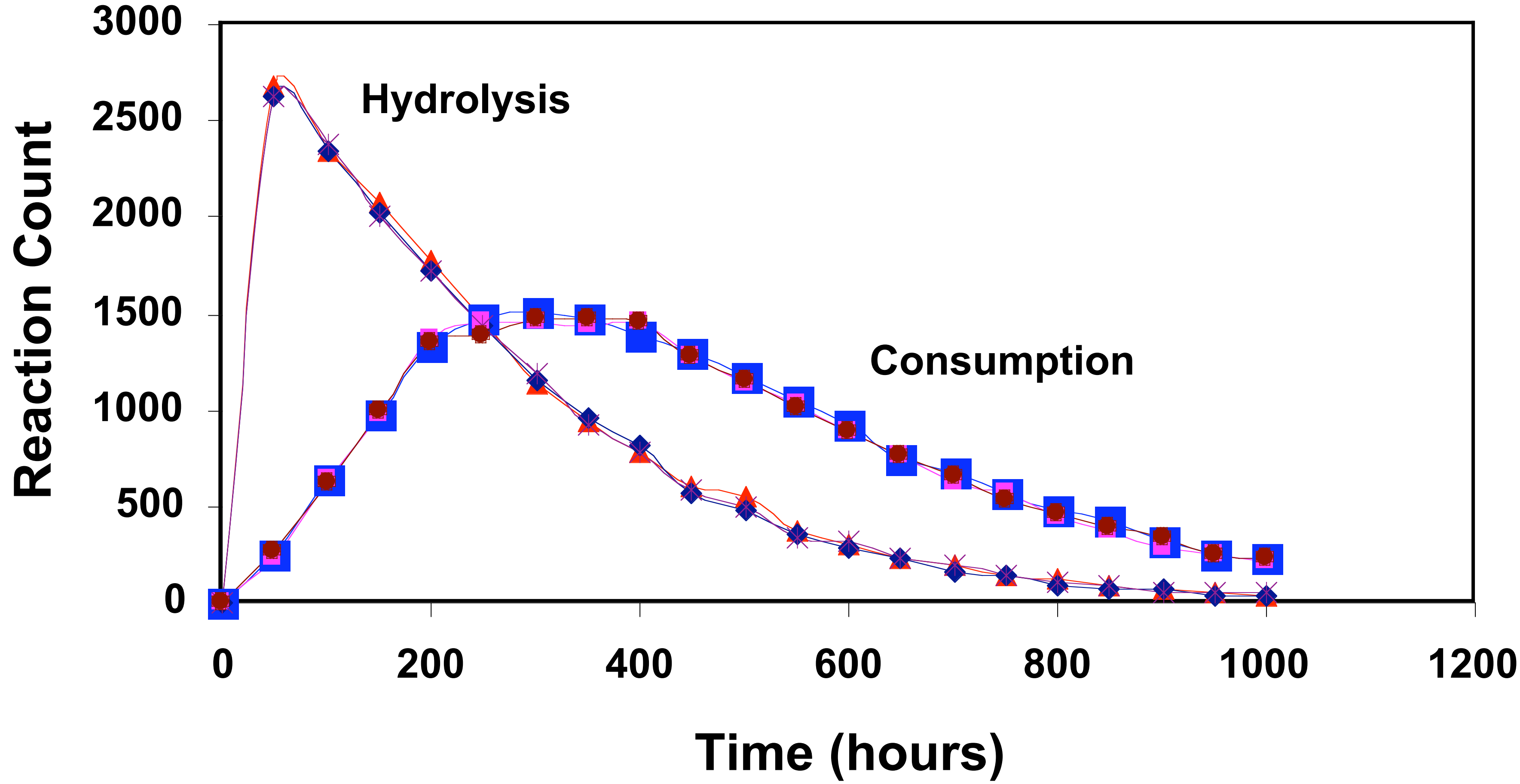


Simulation of protein hydrolysis and consumption

Triplicate runs, random seed = 1, 2, 3

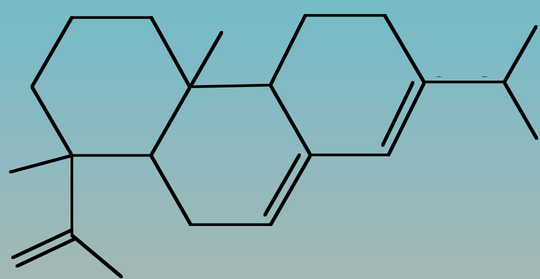


Simulation of protein hydrolysis and consumption
Triplicate runs, random seed = 1, 2, 3

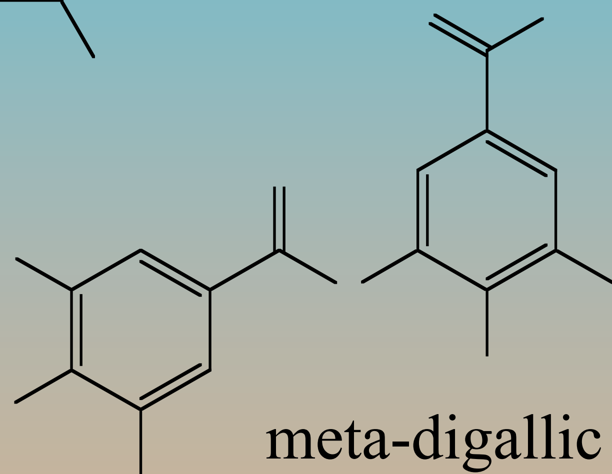


Simulation of protein hydrolysis and consumption
Triplicate runs, random seed 1, 2, 3

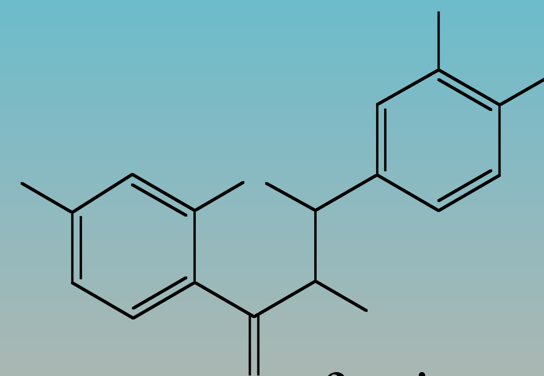
Can we convert terpenes, tannins and flavonoids in soil into NOM ?



abietic acid



meta-digallic acid



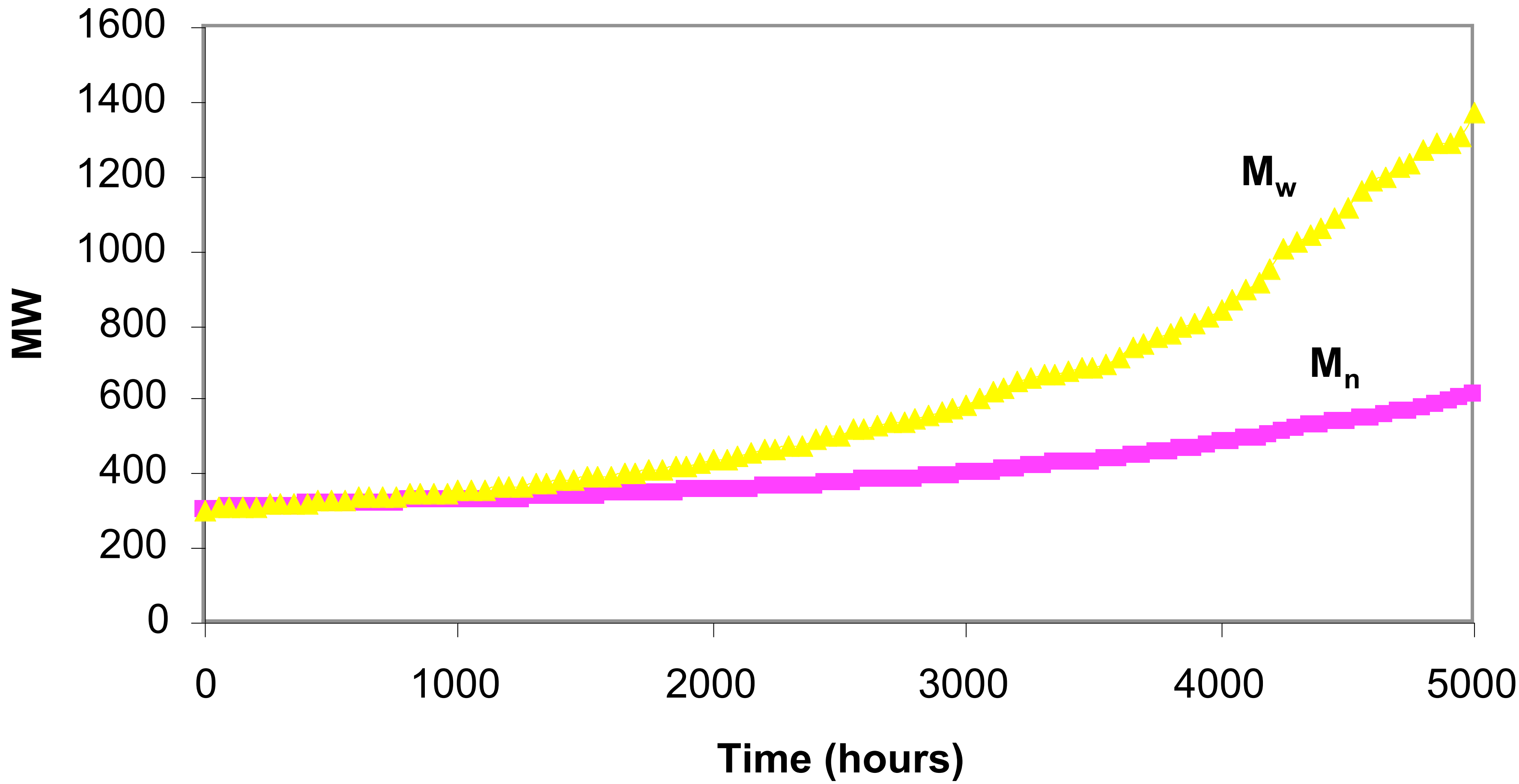
fustin

2000 molecules each

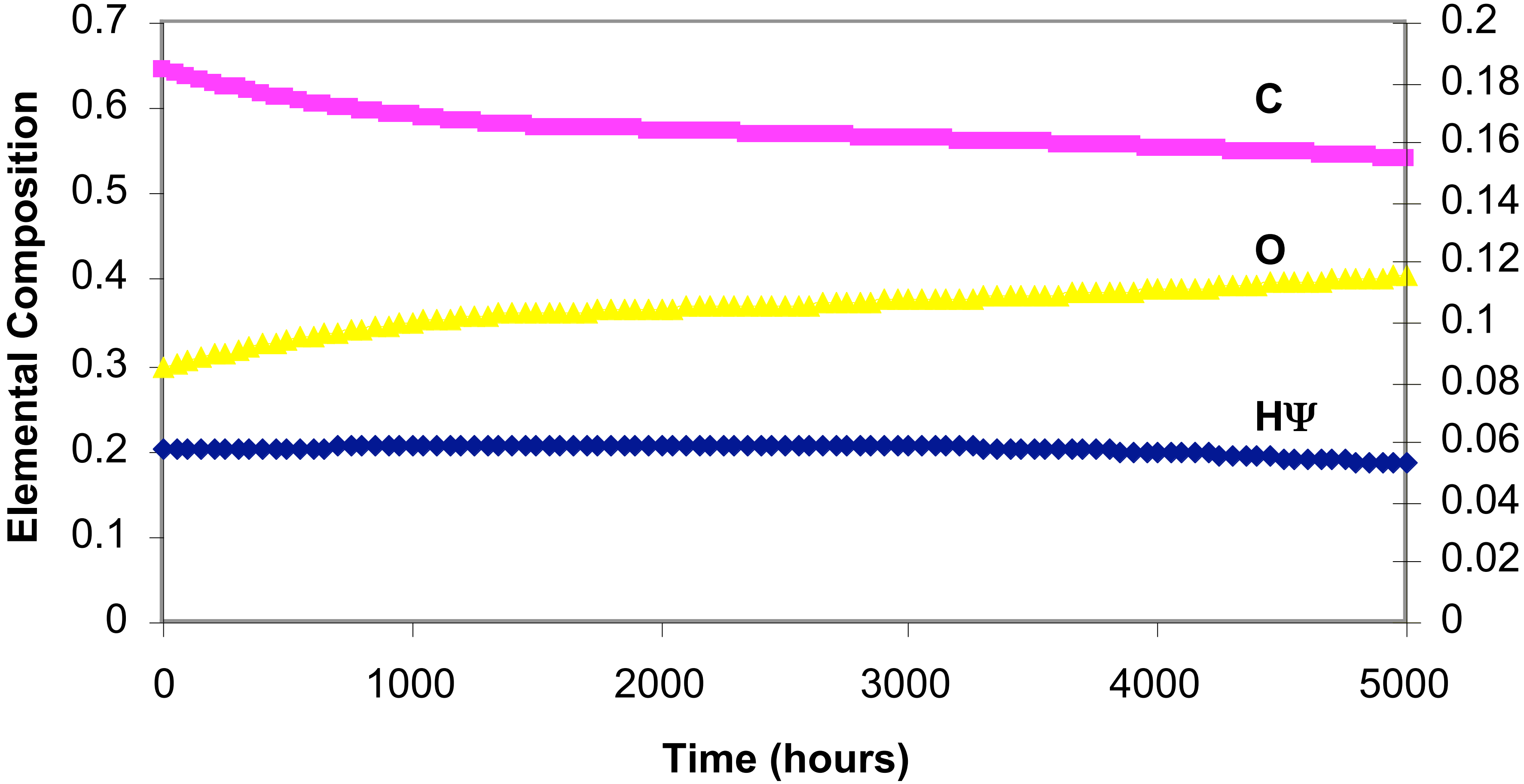
Atmospheric O_2 (0.3 mM) Acidic pH (5.0)

High oxidase activity (0.1) ~5.5 months

Bacterial density 0.01 dark

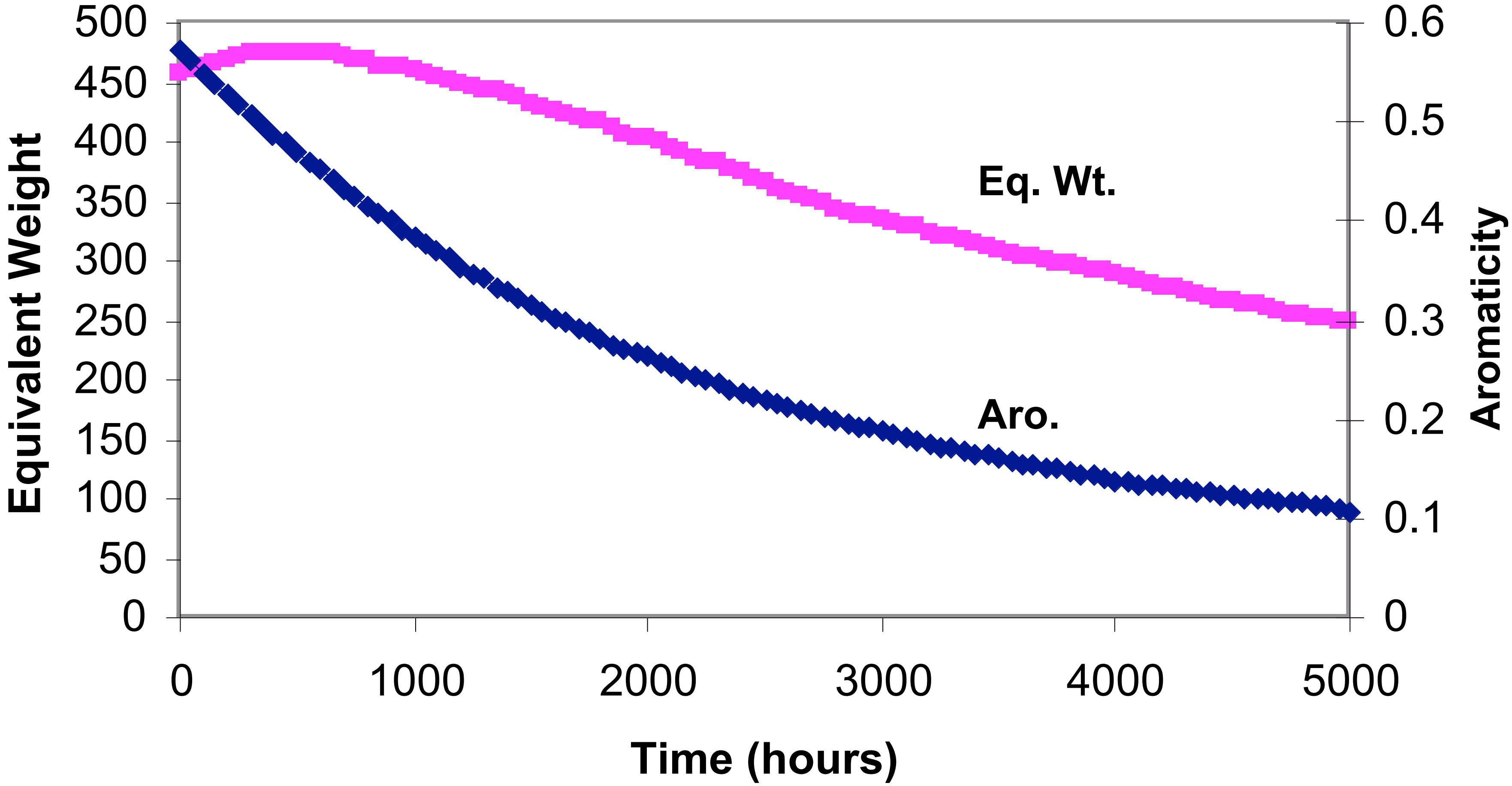


Evolution of NOM from small natural products in oxic soil
Final M_n = 612 amu, M_w = 1374 amu

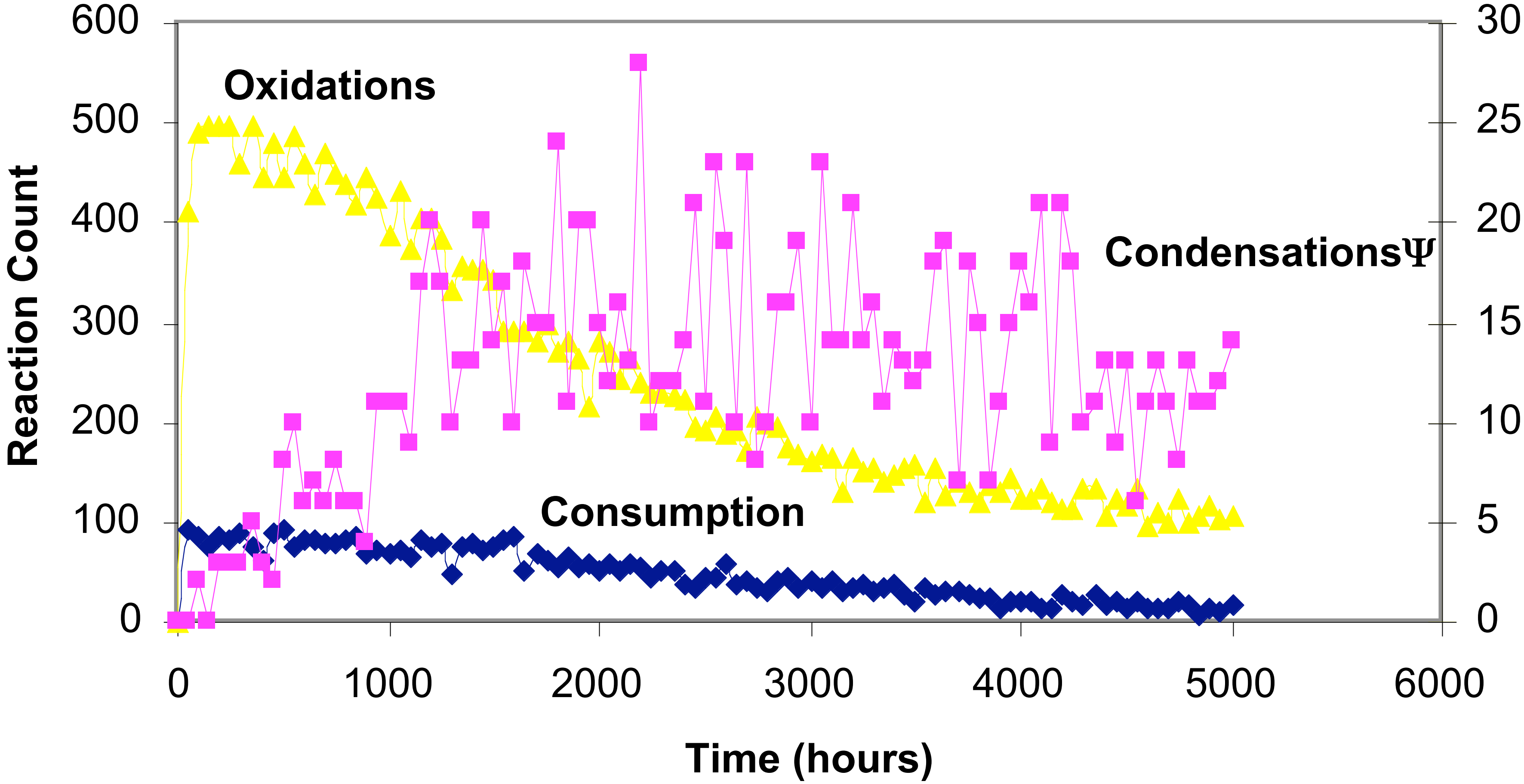


Evolution of NOM from small natural products in oxic soil

Final composition 54% C, 41% O, 5% H



Evolution of NOM from small natural products in oxic soil
Final Eq. Wt. = 247 amu, 11% aromatic C



Evolution of NOM from small natural products in oxic soil

Oxic soil incubation of small natural products

increases M_w by 4X, acidity 2X, O content 30%

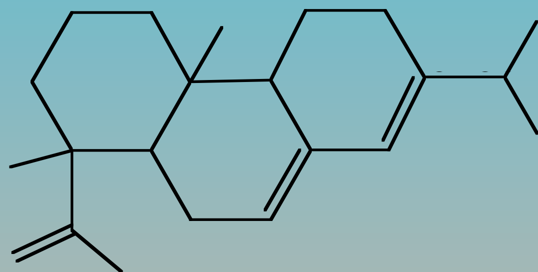
decreases aromaticity 57% Ψ 11%

oxidations enable consumption, condensation

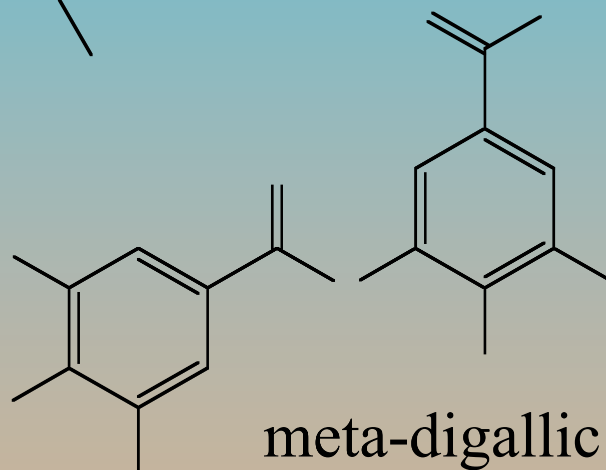
Final composition similar to fulvic acid:

- 54% C, 41% O, 5% H
- Mn = 612 amu, Mw = 1374 amu
- Eq. Wt. = 247 amu, 11% ‘aromaticity’

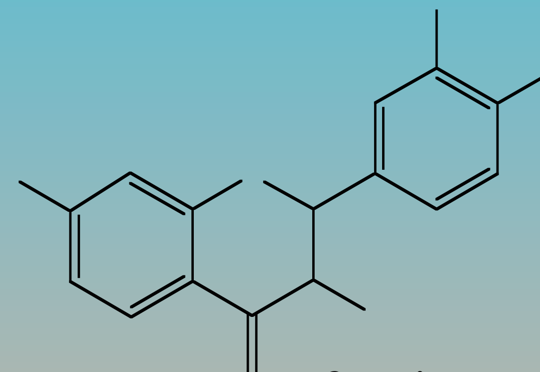
How is this conversion to NOM affected by lowering the O_2 and oxidase levels?



abietic acid



meta-digallic acid



fustin

2000 molecules each

Reduced O_2 (0.1 mM)

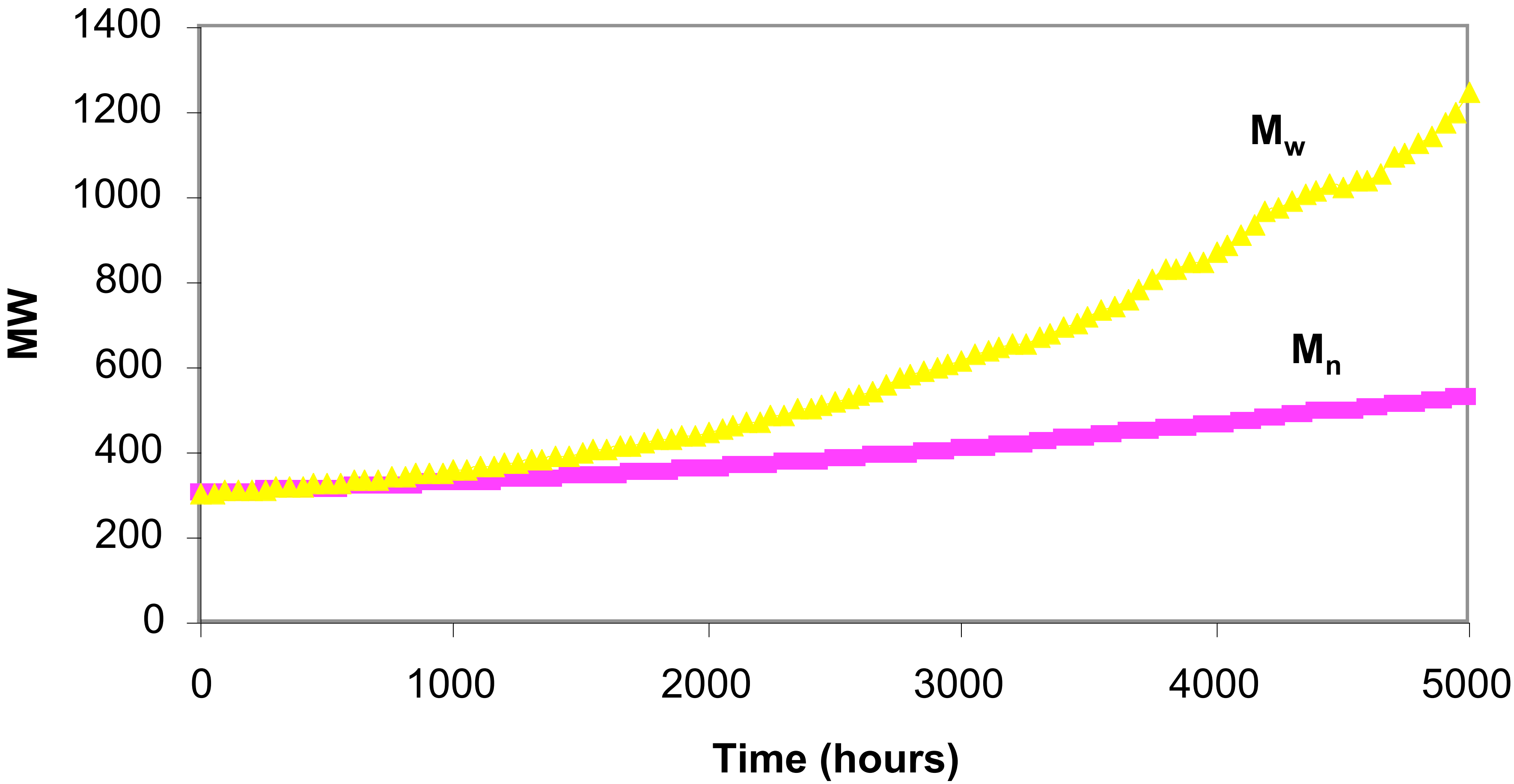
Low oxidase activity (0.03)

Bacterial density 0.01

Acidic pH (4.0)

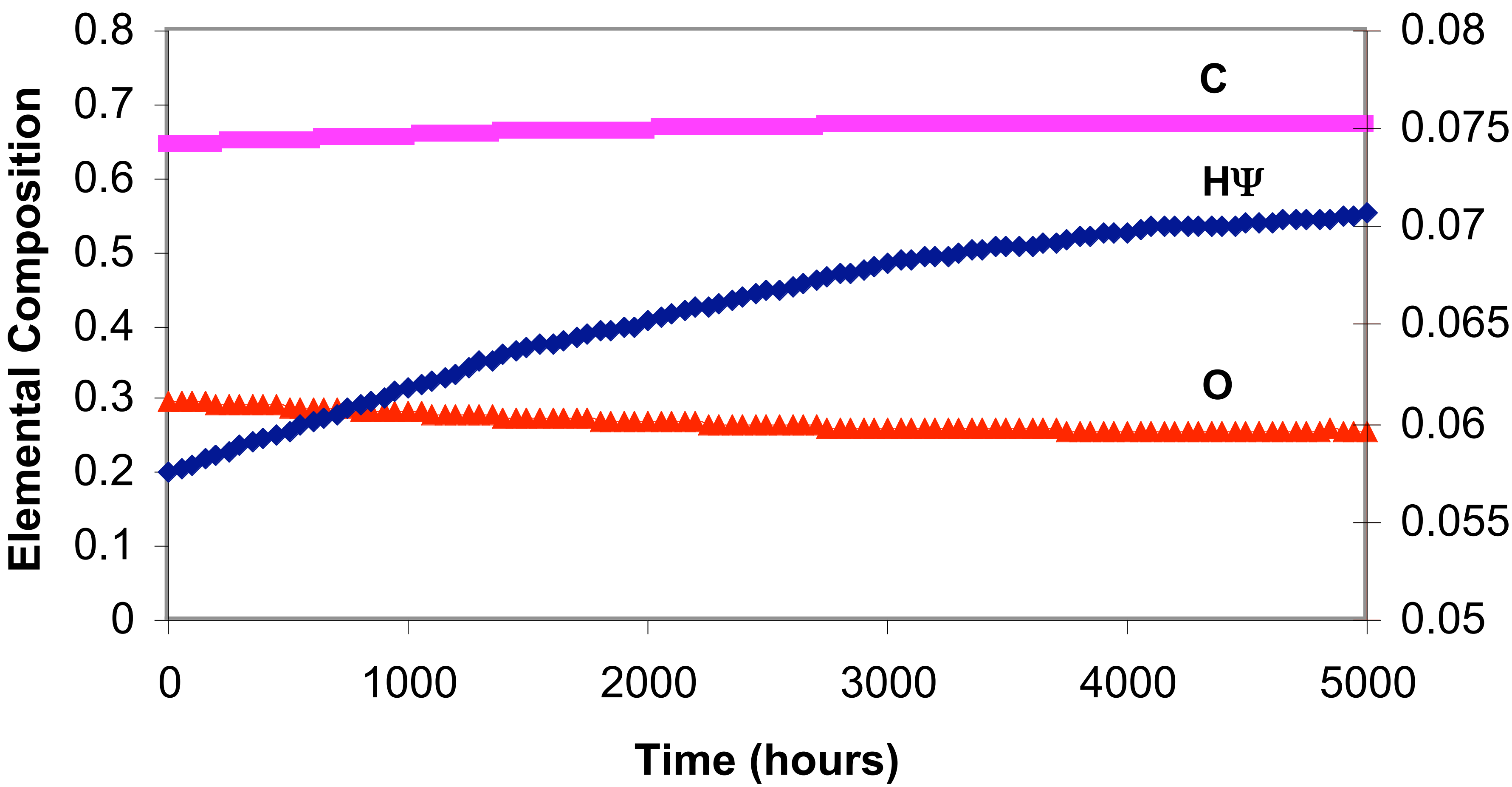
~5.5 months

dark

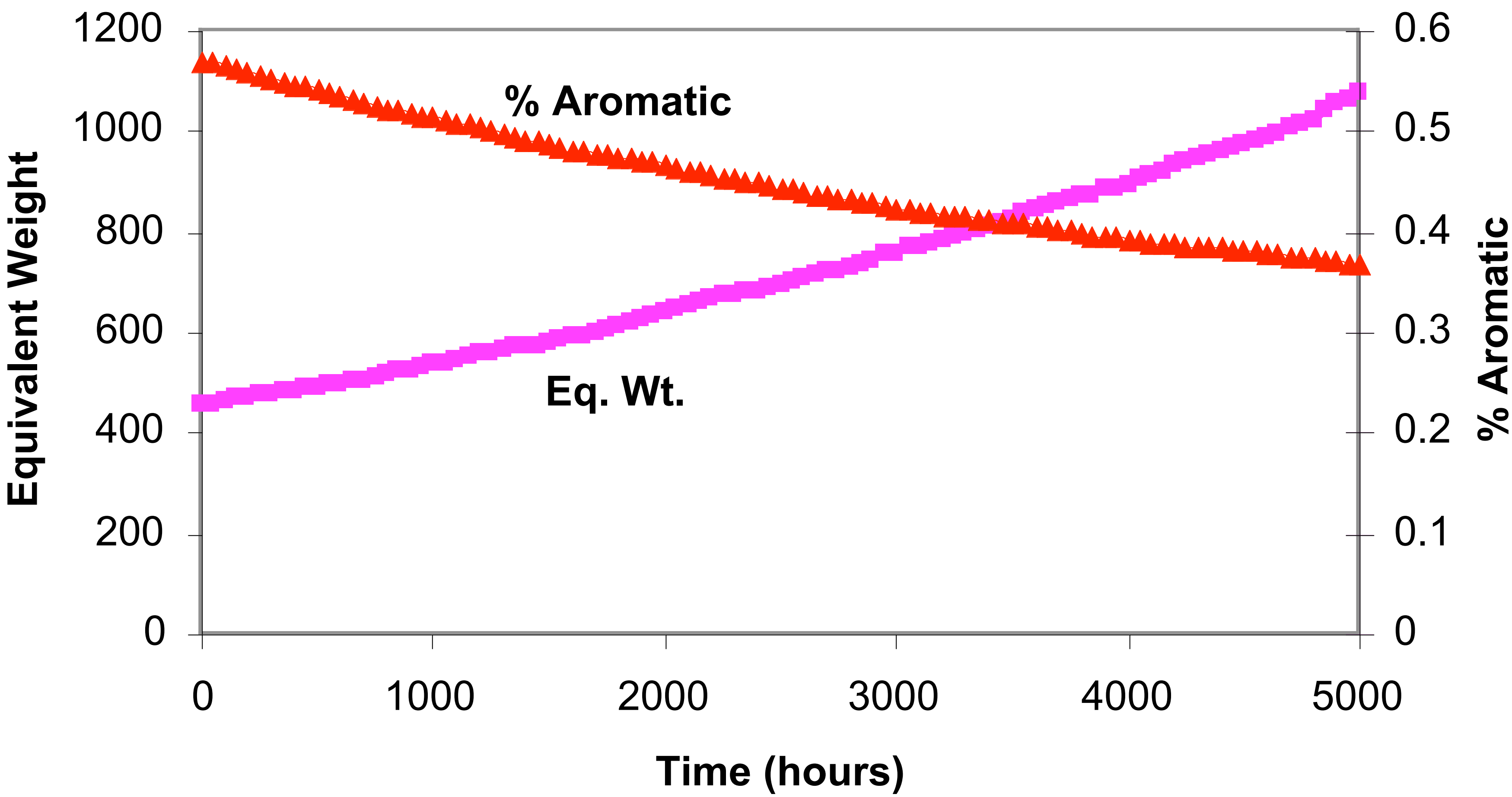


Evolution of NOM from small natural products in low-O_2 soil

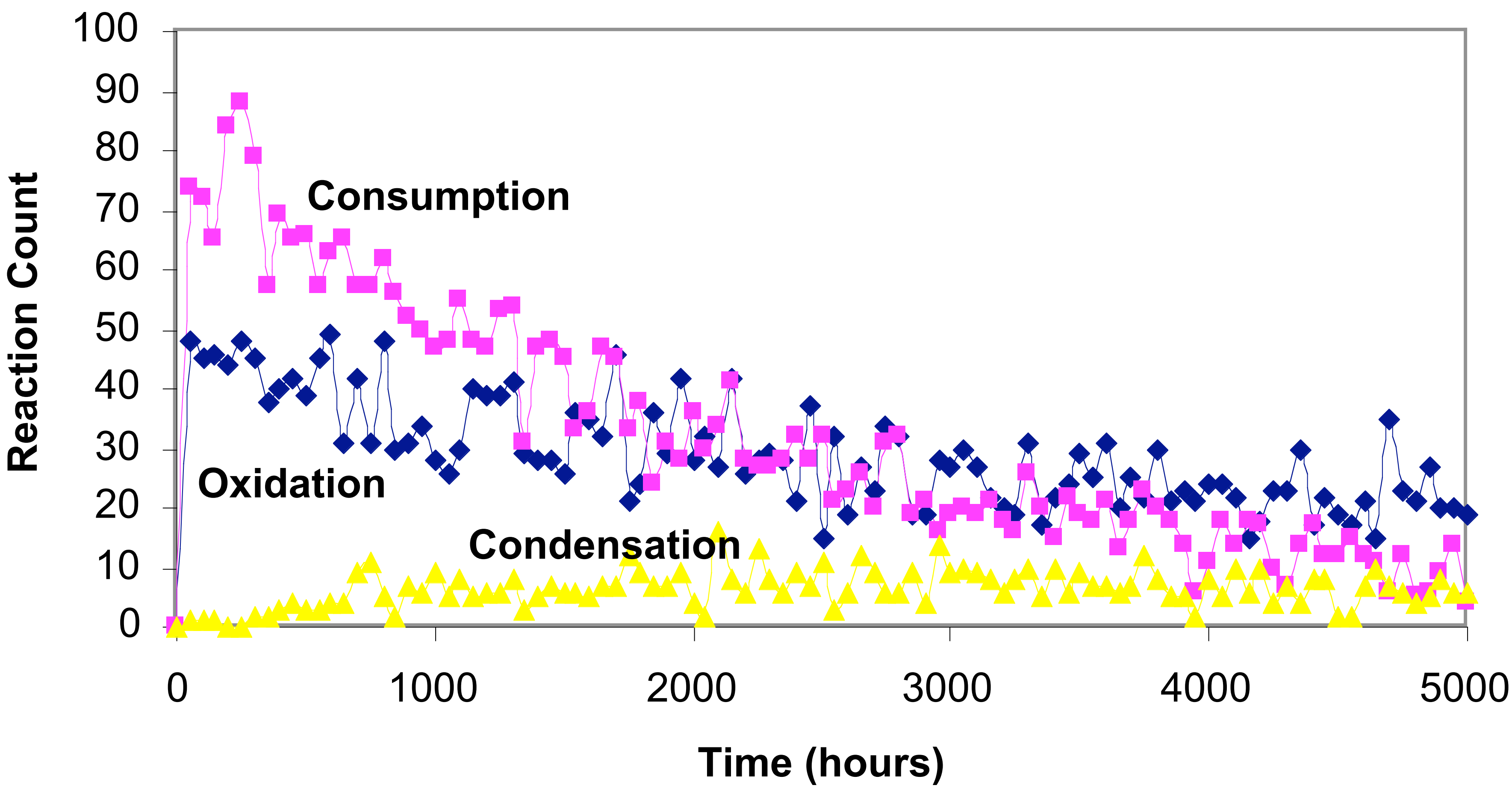
Final M_n = 528 amu, M_w = 1246 amu



Evolution of NOM from small natural products in low O_2 soil
Final composition 67% C, 26% O, 7% H



Evolution of NOM from small natural products in low O_2 soil
Final Eq. Wt. = 1075 amu, 37% aromatic C



Evolution of NOM from small natural products in low O2 soil
Consumption ~30% lower, oxidation 7X lower,
condensation 30X lower than in oxic soil.

Low O_2 soil incubation of small natural products

increases M_w by 4X, H content 25%
decreases aromaticity 57% Ψ 37%

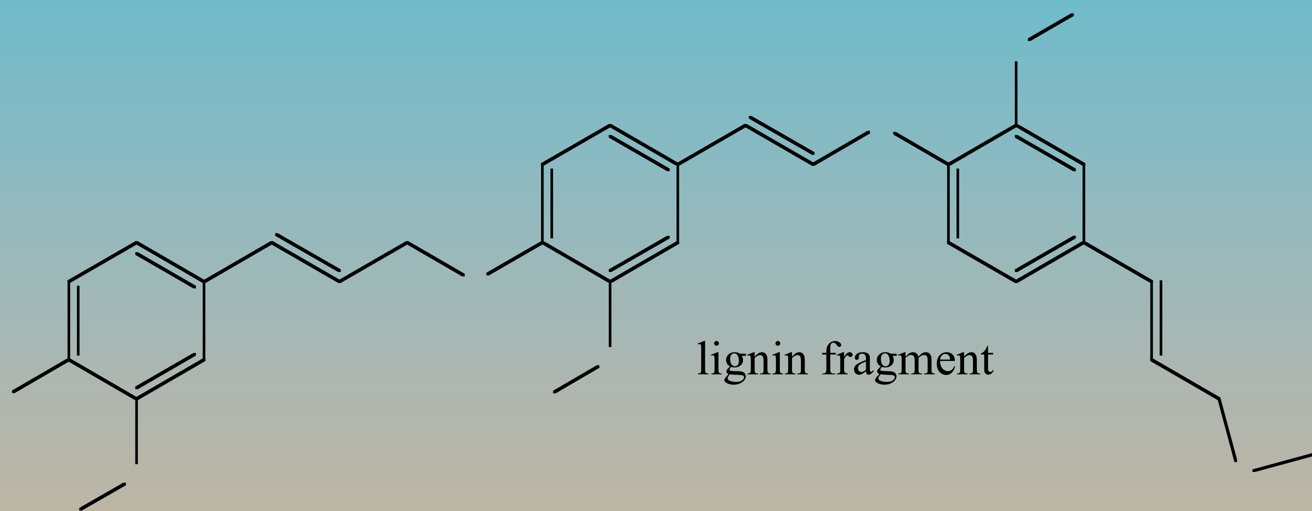
Final composition more reduced, higher UV ,, less charged (soluble) than fulvic acid:

67% C, 26% O, 7% H

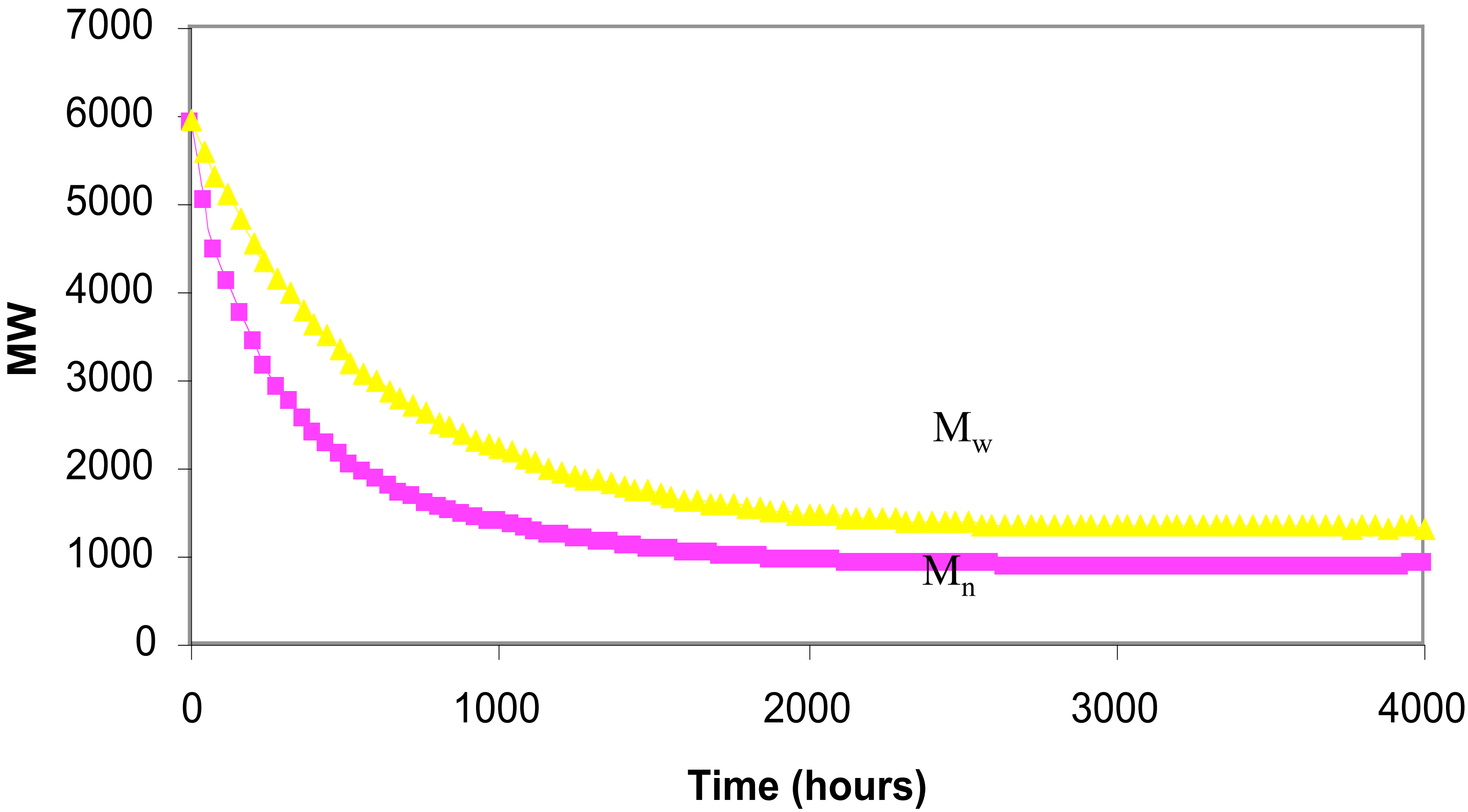
Mn = 612 amu, Mw = 1374 amu

Eq. Wt. = 1075 amu, 37% ‘aromaticity’

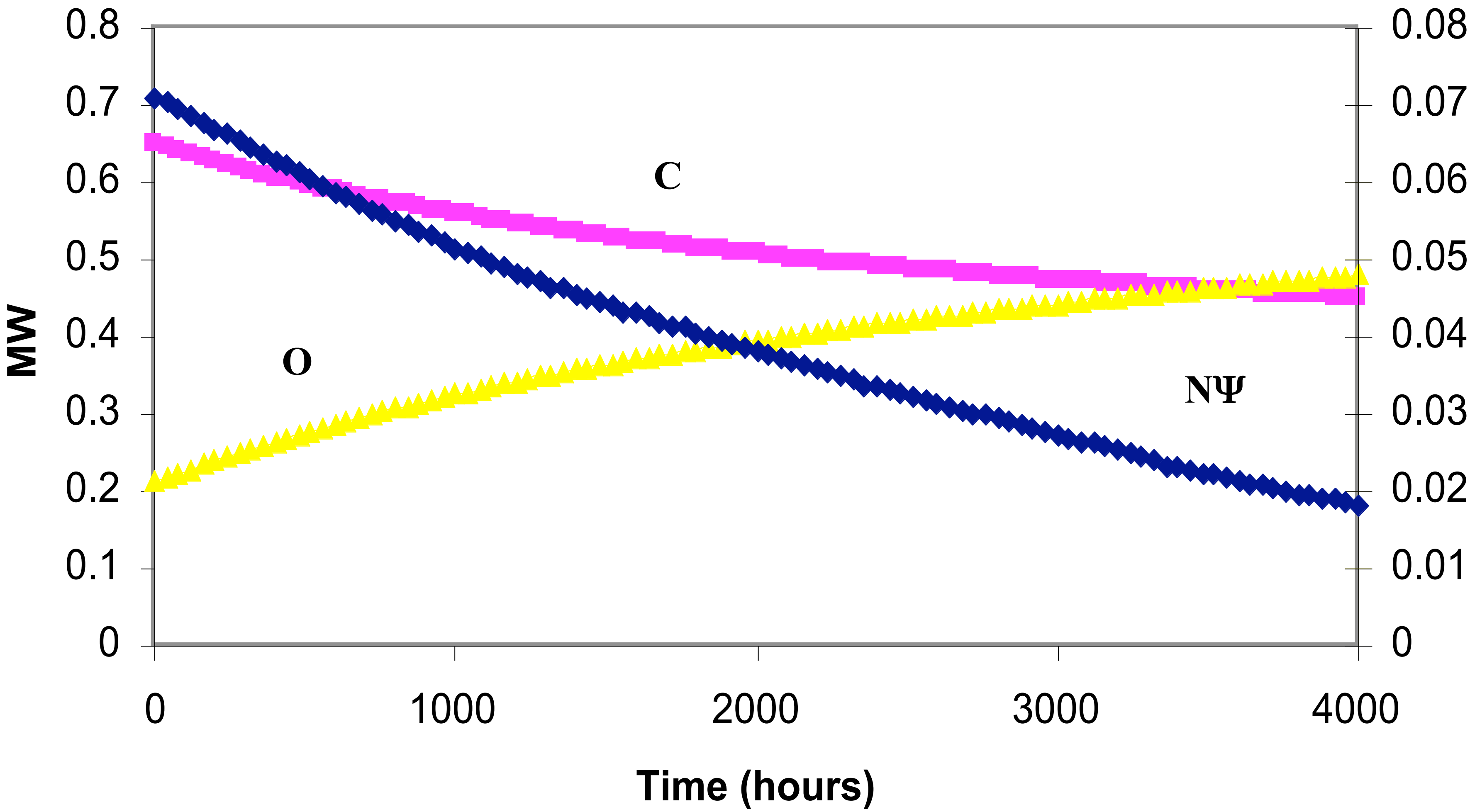
Trial: Can we convert lignin and protein molecules into NOM ?



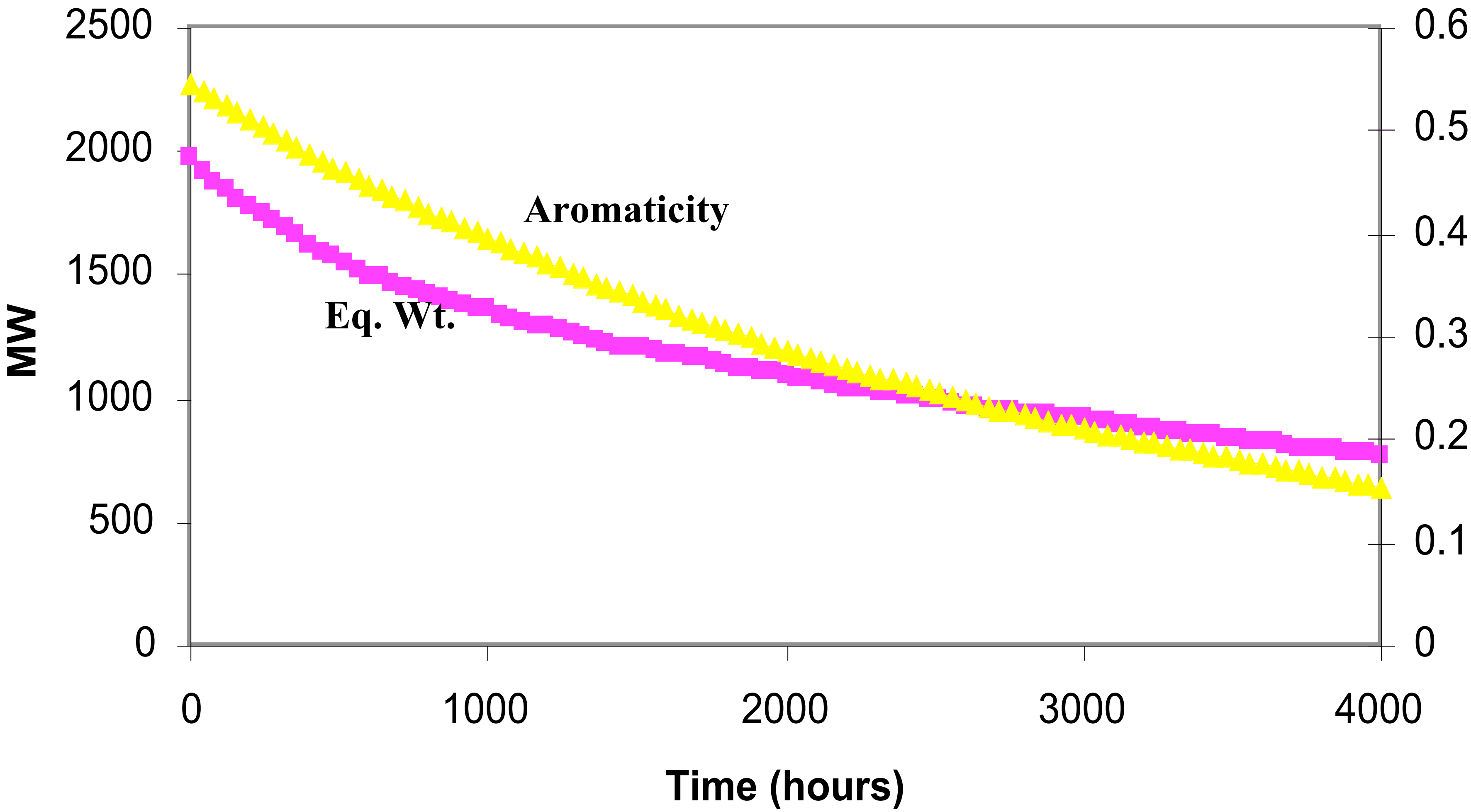
Atmospheric O_2 (0.3 mM)	Moderate light ($2x10^{-8}$ E cm^{-2} hr^{-1})
Neutral pH (7.0)	24.8 ^oC
Lower enzyme activity (0.01)	Moderate bacterial density (0.02)
4 months reaction time	400 molecules lignin and protein



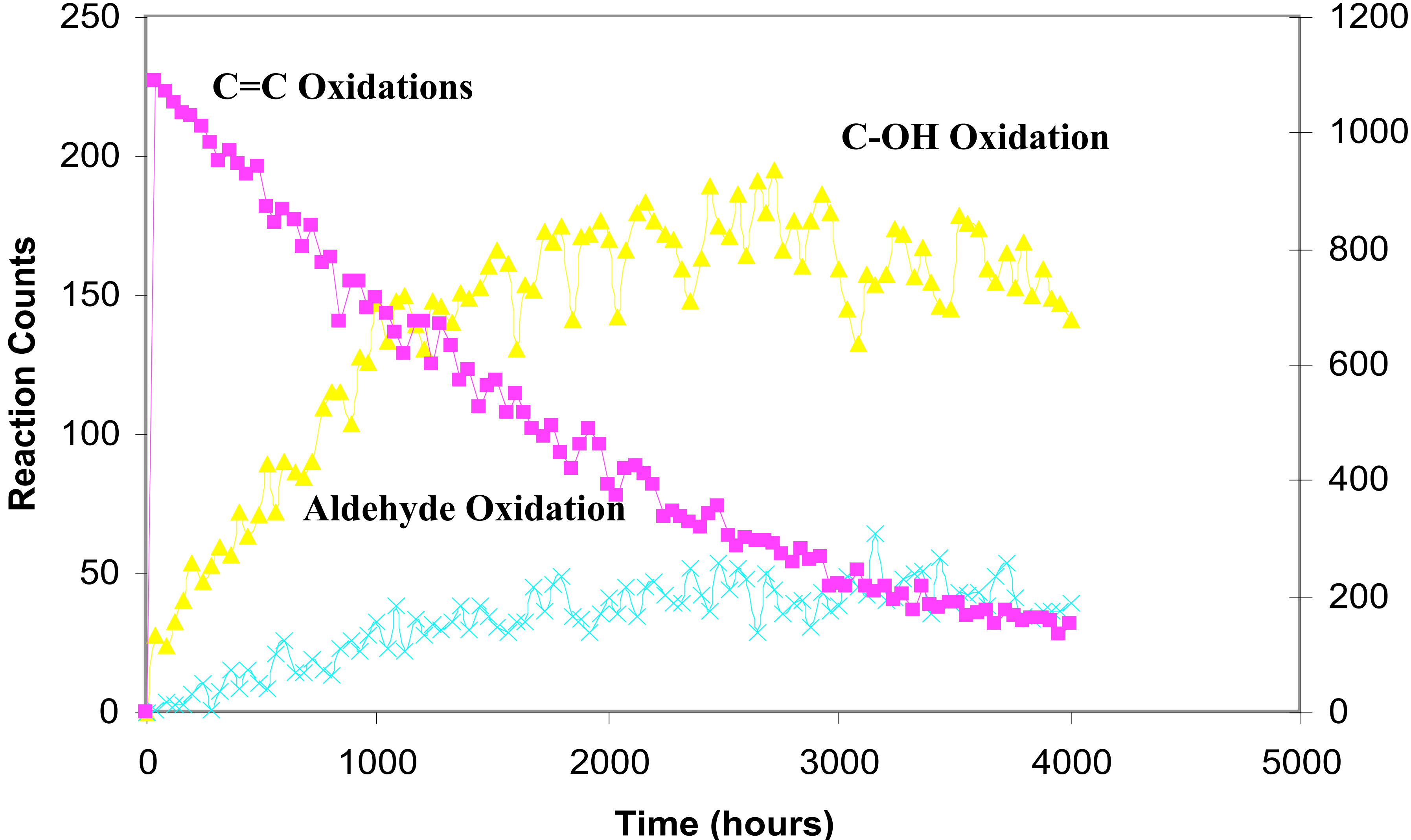
Evolution of NOM from lignin and protein in surface water
Final M_n = 902 amu, M_w = 1337 amu
(Mass distribution is log normal.)



Evolution of NOM from lignin and protein in surface water
Final composition 45% C, 48% O, 5.2% H, 1.8% N



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

Surface water degradation of biopolymers

Decreases M_n by 6X, aromatic C by 3X

Increases acidity 3X, O content 100%

Final composition similar to ‘hydrophilic’ NOM:

- 45% C, 48% O, 5% H, 1.8% N
- Mn = 902 amu, Mw = 1337 amu
- Eq. Wt. = 772 amu, 15% ‘aromaticity’

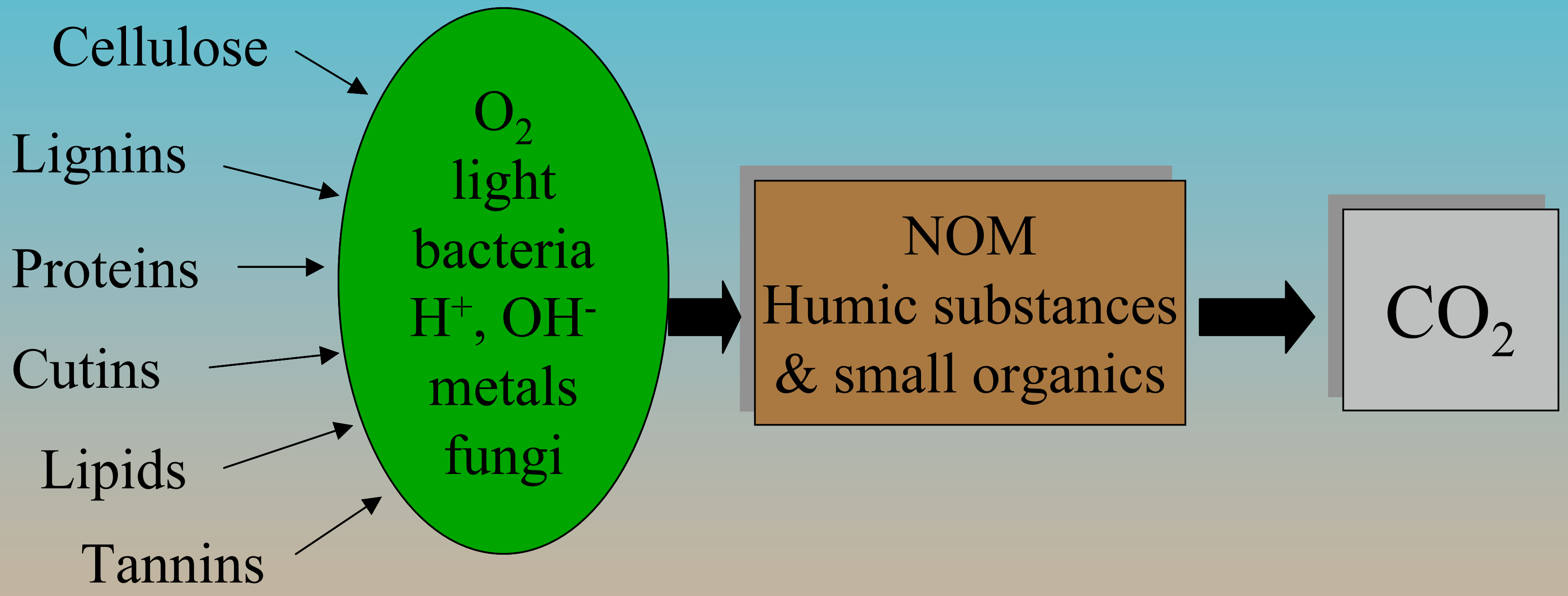
Stochastic synthesis

- 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
  - pK_a, K_{ow}, $K_{Cu\text{-}L}$
  - UV, IR, nmr spectra
- Spatial and temporal controls
  - Diurnal and seasonal changes
  - 'continuous reactor'
  - Spatial modeling of soils, streams
- Data mining capabilities

Stochastic Synthesis of NOM



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

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Collaborating Scientists

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