Stochastic Synthesis of Natural Organic Matter

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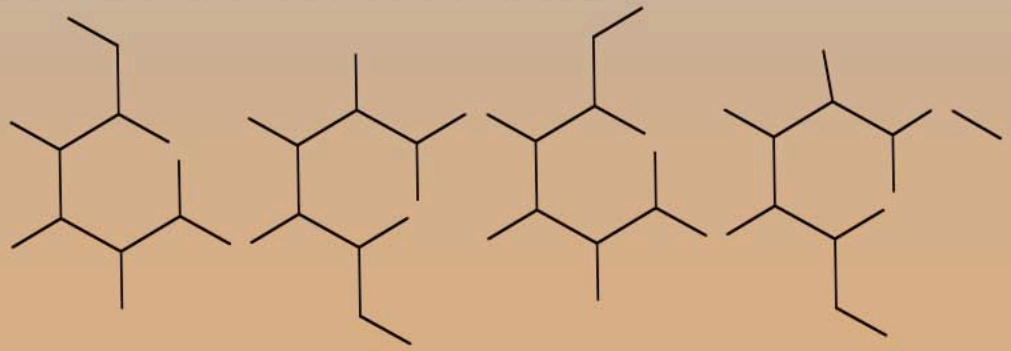
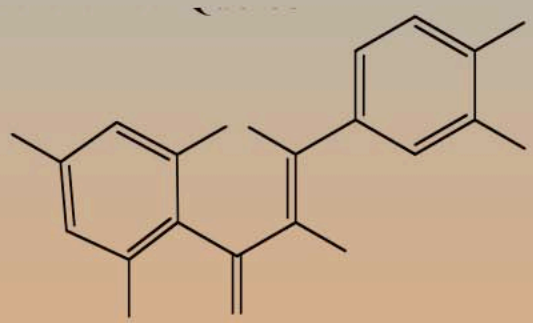
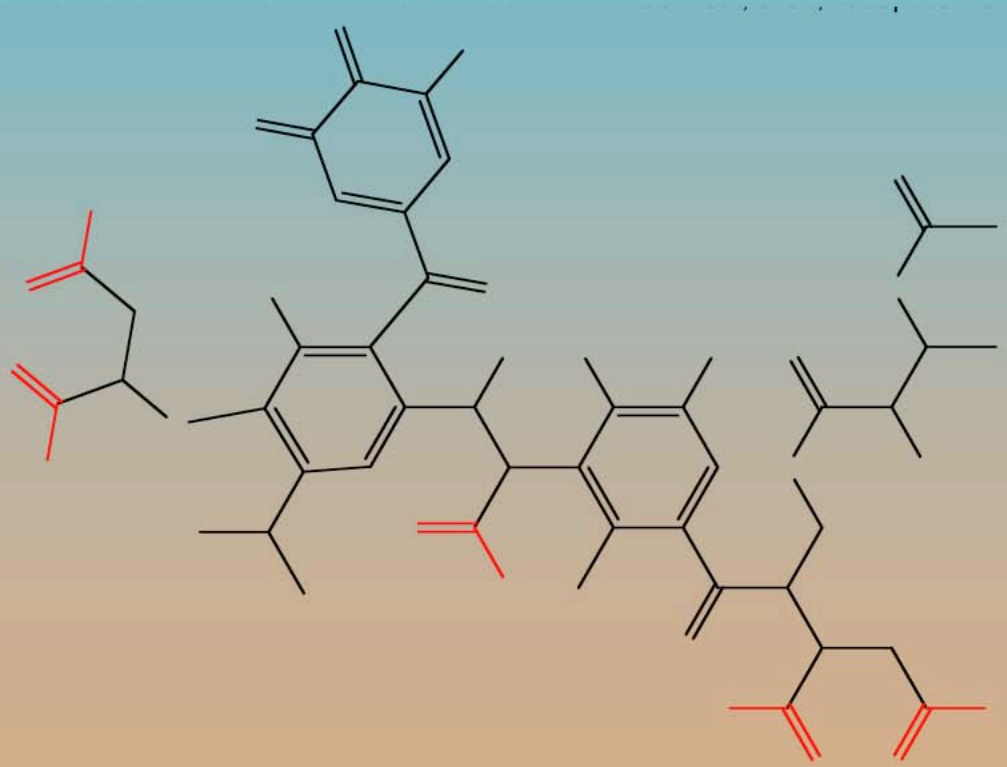
What is NOM? Sources:

- Plant and animal decay products
  - Terrestrial- woody and herbaceous plants
  - Aquatic- algae and macrophytes
- Structures
  - cellulose, lignins, tannins, cutin
  - proteins, lipids, sugars





What is NOM? Composition



45-55 Wt% Carbon

35-45 Wt% Oxygen

3-5 Wt% Hydrogen

1-4 Wt% Nitrogen

Traces P, S

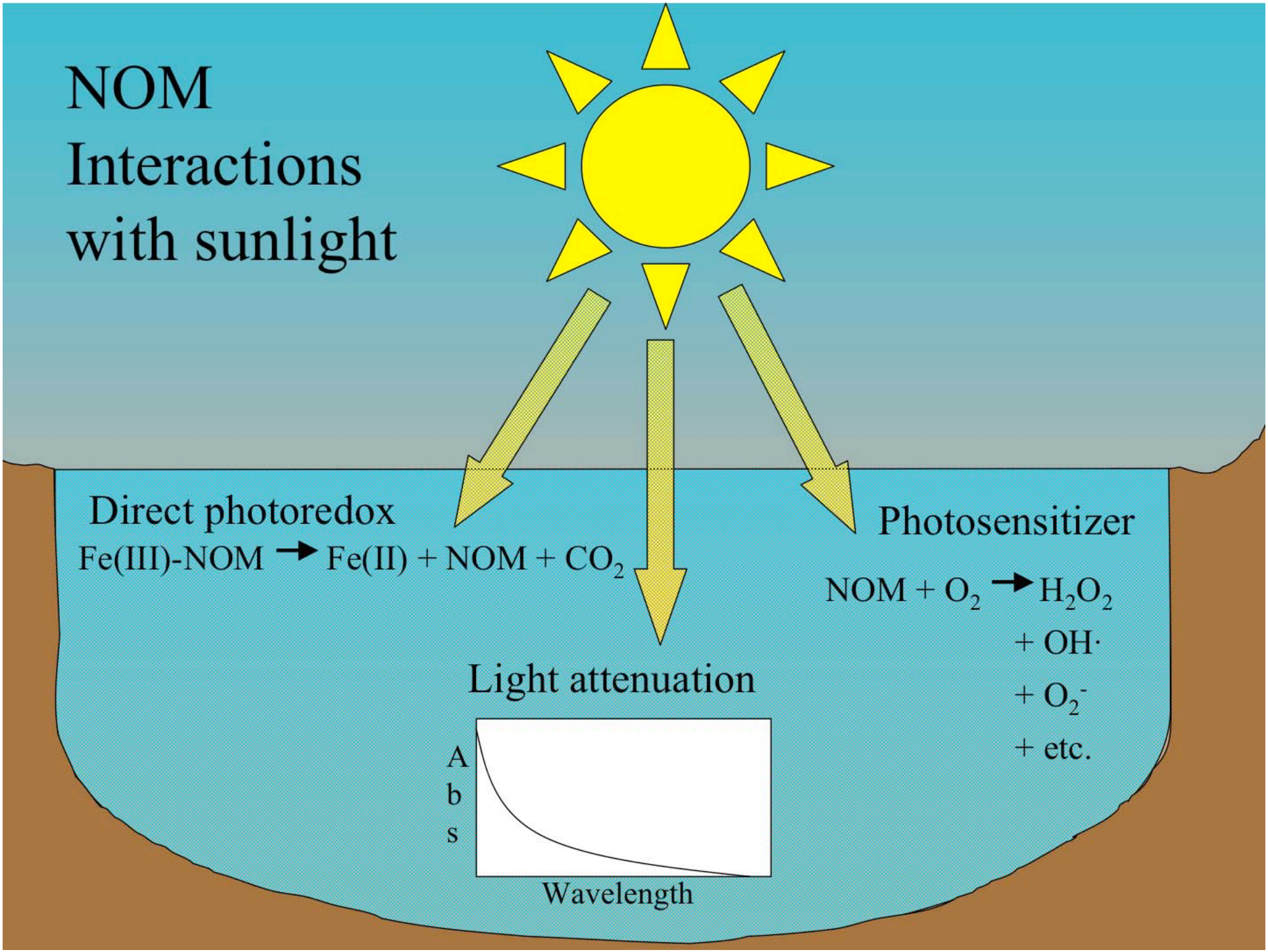
MW 200-20,000 amu

Equiv. Wt. 200-400 amu

10-35% aromatic C

What is NOM?

A mixture of degradation
and repolymerization products
from aquatic and terrestrial organisms
which is heterogeneous with respect
to structure and reactivity.


NOM
Interactions
with sunlight
Direct photoredox
Fe(III)-NOM → Fe(II) + NOM + CO2
Photosensitizer
NOM + O2 → H2O2
+ OH·
+ O2-
+ etc.
Light attenuation
Abs
Wavelength

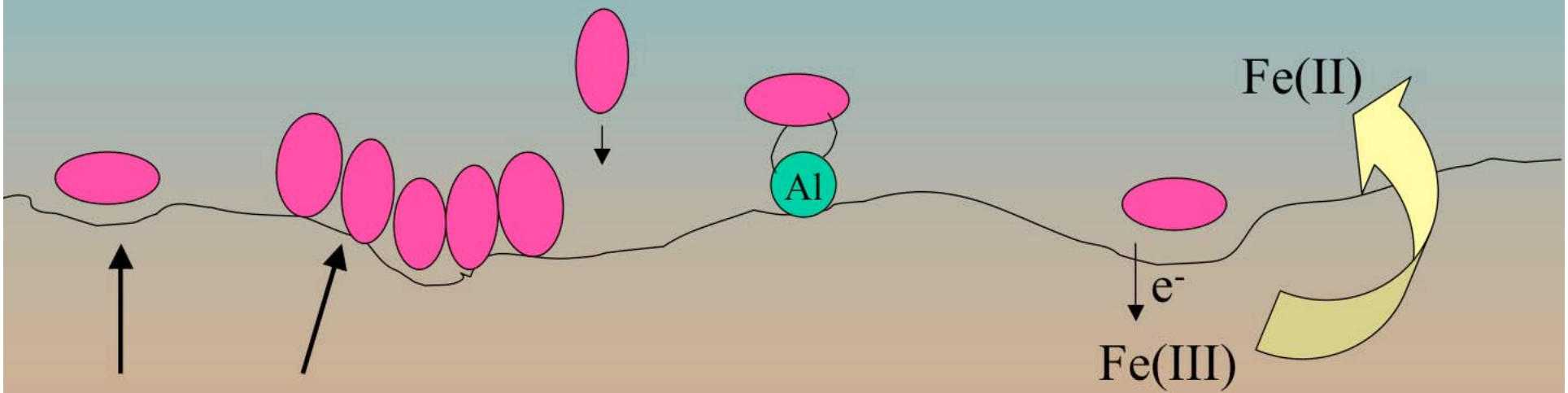
NOM Interactions with mineral surfaces

Adsorption

Hemi-micelle formation

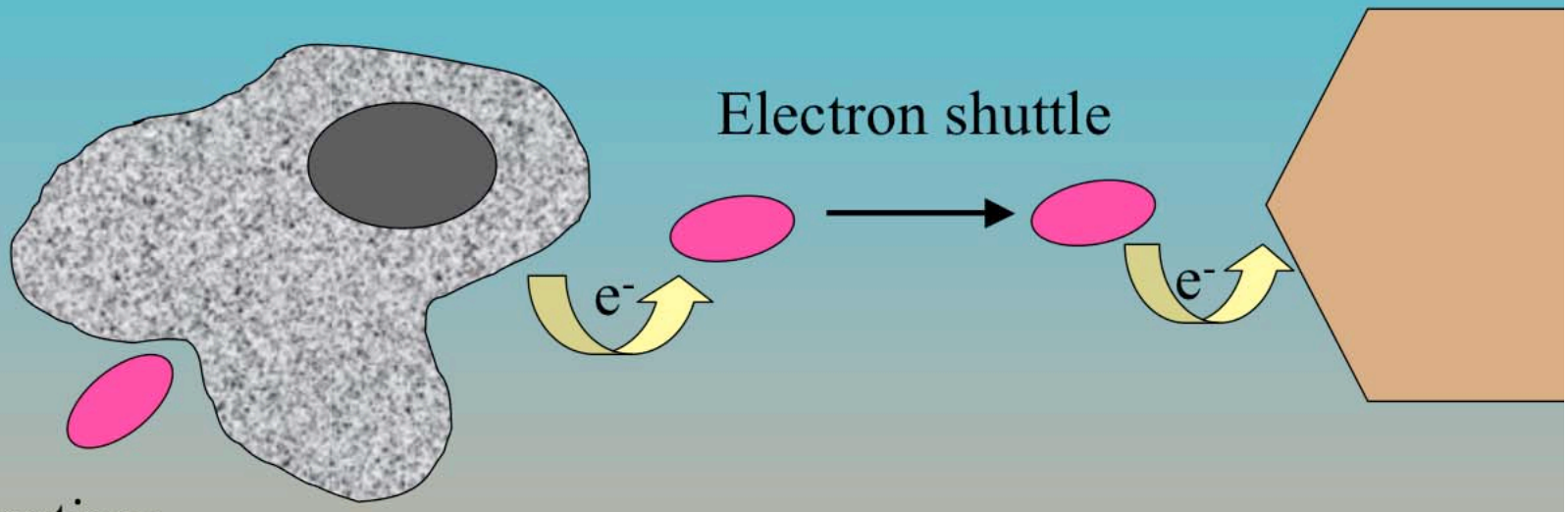
Acid or complexing dissolution

Reductive dissolution

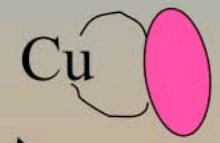


Adsorbed NOM coatings impart negative charge and create a hydrophobic microenvironment

NOM Interactions with microbes



Ingestion:
Energy and
Nutrients



Cu^{2+}

Metal ion complexation
and de-toxification

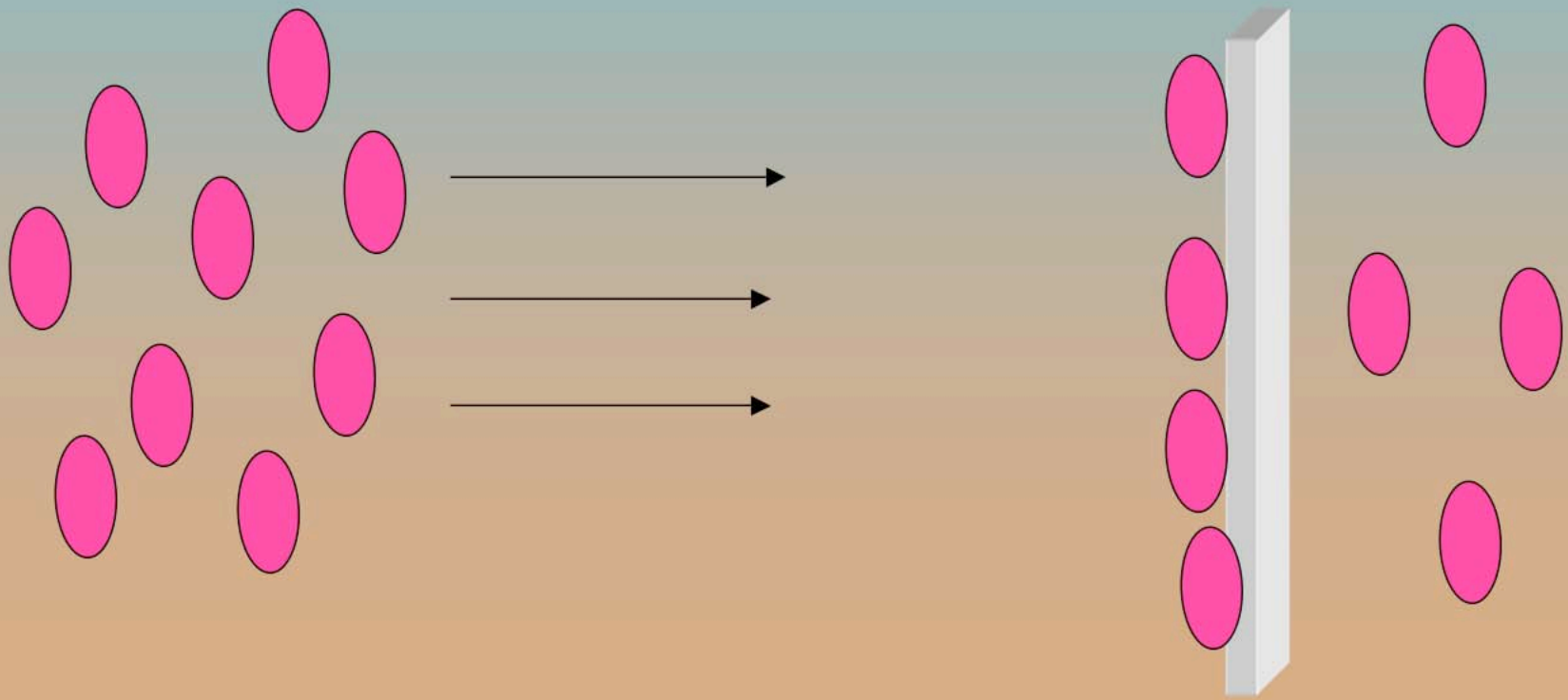
NOM Interactions with pollutants

Binding to dissolved NOM increases pollutant mobility

NOM in water treatment

+ HOCl

$CHCl_3 + CHCl_2Br + CCl_3COOH$
and other chlorinated by-products



Why study NOM?

Natural ecosystem functions

Nutrition, buffering, light attenuation

Effects on pollutants

Radionuclides, metals, organics

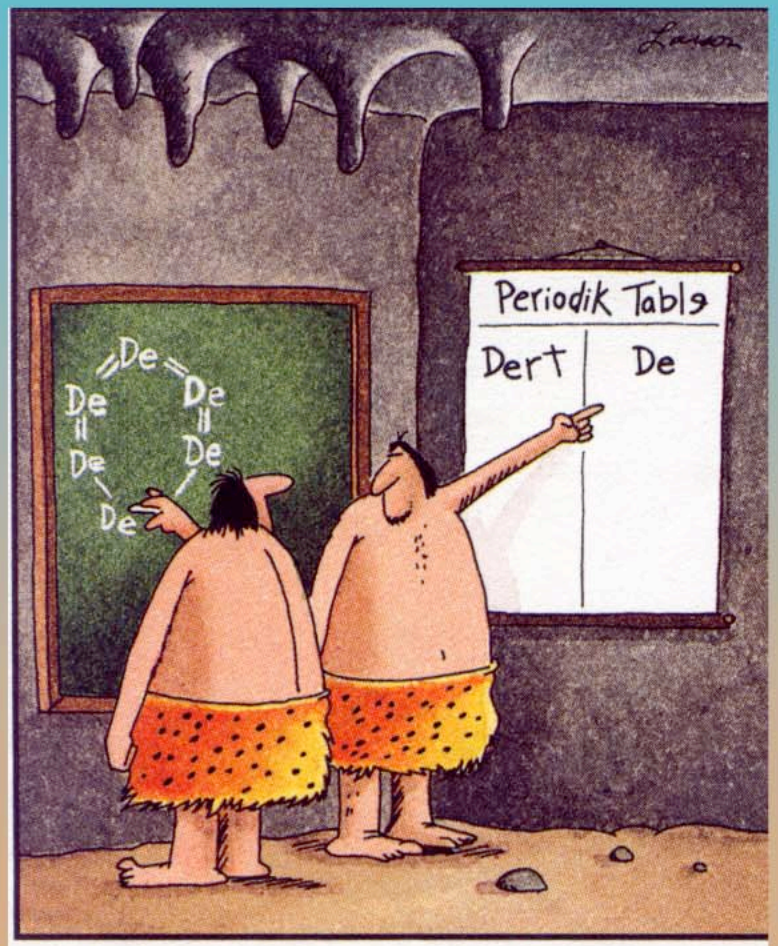
Water treatment

DBP's, membrane fouling, Fe solubility

Carbon cycling & climate change

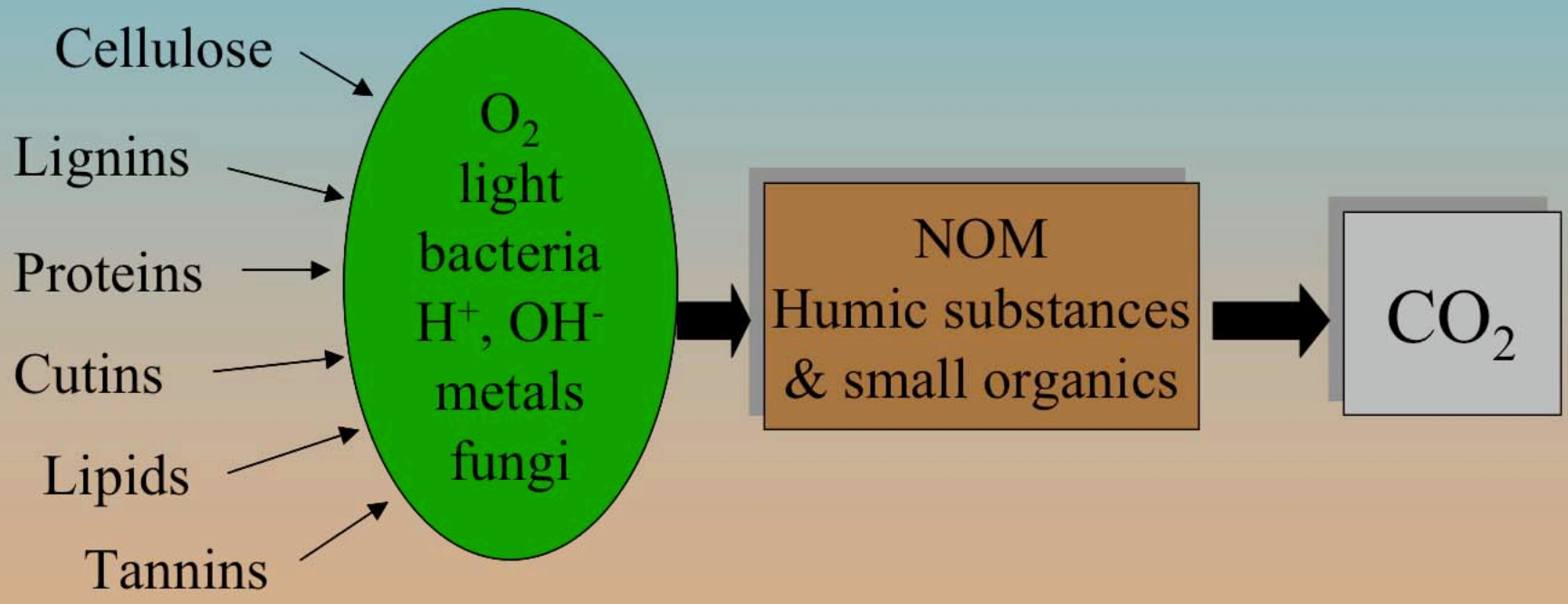
NOM Questions:

- 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 Deterministic Reaction Kinetics

For a pseudo-first order reaction

$$\mathbf{R = dC/dt = k' C}$$

R = rate (change in molarity per unit time)

C = concentration (moles per liter)

k' = pseudo-first order rate constant (units of time^{-1})

Based on macroscopic concentrations

Deterministic Reaction Kinetics: Solve a system of ODE's

- Begin with initial C_i for each of N compounds, k_j for each of M reactions
- Apply Runge-Kutta or predictor-corrector methods to calculate $)C_i$ for each time step (use Stiff solvers as needed)
- Repeat for desired length of simulation, obtaining results as C_i versus time

Problem w/ ODE approach: Size and Computation Time

- Assuming N > 200 (different molecules)
- Assume M = 20 x N (20 reactions per molecule)
- Total set of >4000 very stiff ODE's is impractical (transport eqns not included)

Problem w/ODE Approach: Knowledge Base

- Structures of participating molecules unknown
- Pertinent reactions unknown
- Rate constants k_j unknown

Simulating NOM Synthesis Probabilistic Reaction Kinetics

For a pseudo-first order reaction

$$\mathbf{P = k' \_t}$$

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

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

Based on individual molecules

Stochastic algorithm: Initialization

- Create initial pseudo-molecules (objects)
  - Composition (protein, lignin, cellulose, tannin)
  - Location (top of soil column, stream input)
  - Input function (batch mode, continuous addition, pulsed addition)
- Create environment
  - specify pH, light, enzyme activity, bacterial density, humidity, T^{o}, flow regime

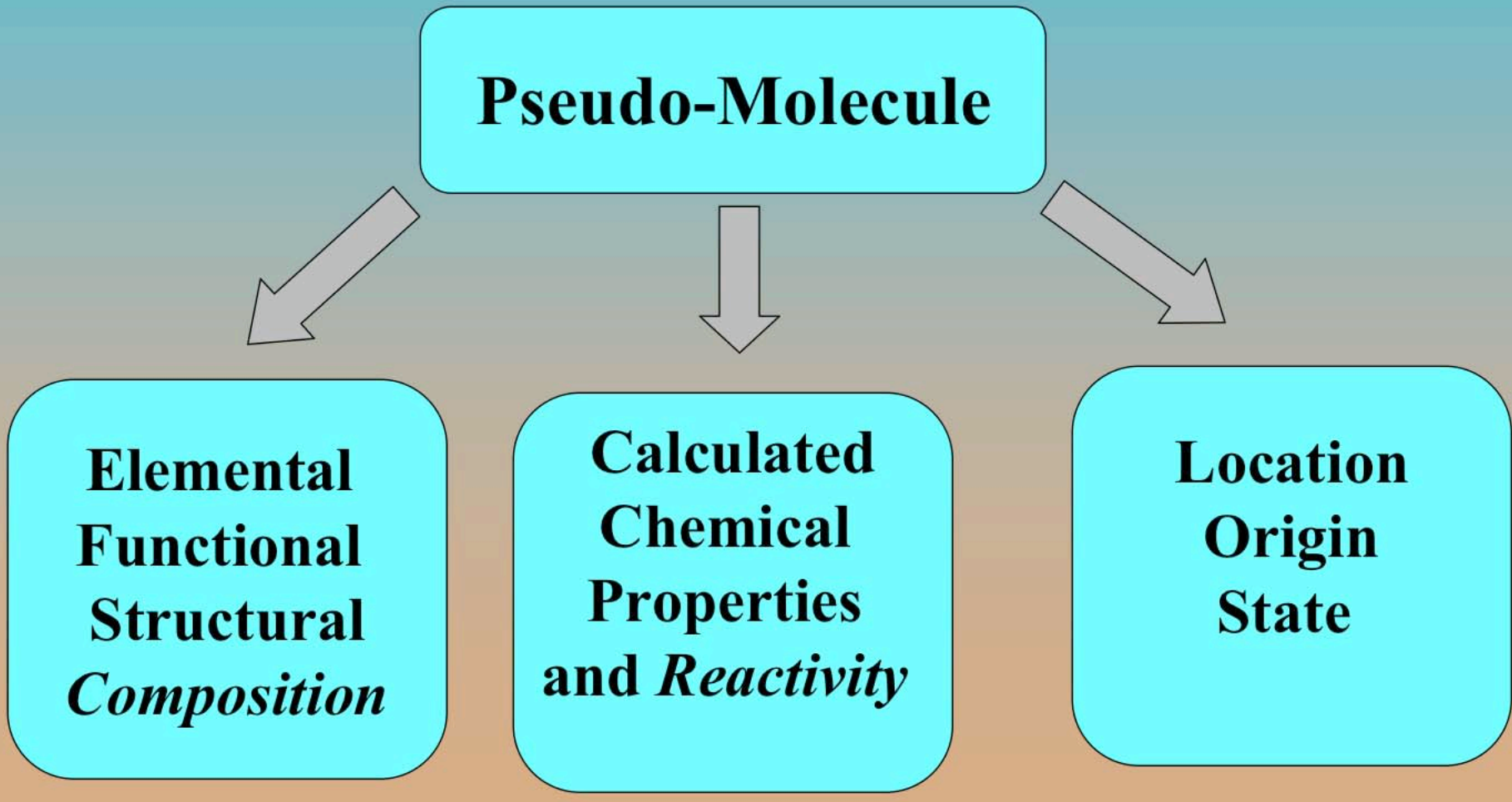
Stochastic Algorithm: Reaction Progress

- Chemical reaction: For each time-slice, each pseudo-molecule
  - determine which reaction (if any) occurs
  - modify structure, reaction probabilities
- Transport: For each time-slice, each pseudo-molecule
  - Determine mobility
  - Modify location, reaction probabilities
- Repeat, warehousing ‘snapshots’ of pseudo-molecules and aggregate statistics

Stochastic Algorithm: Advantages

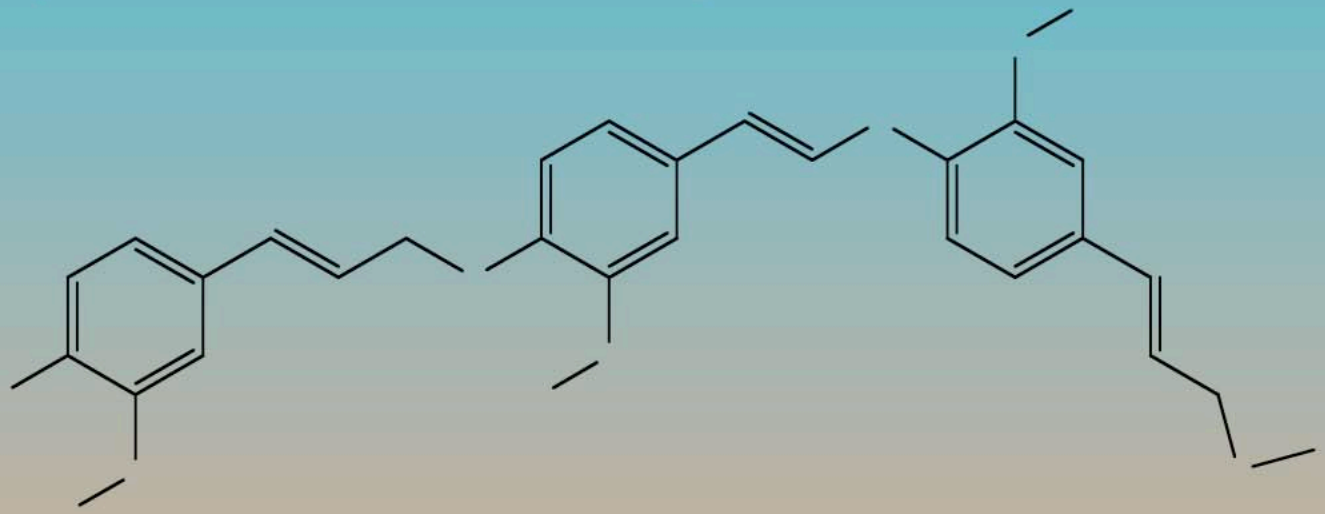
- Computation time increases as # molecules, not # possible molecules
- Flexible integration with transport
- Product structures, properties not pre-determined

Stochastic synthesis: Data model



Average Lignin Molecule:

Oligomer of 40 coniferyl alcohol subunits



Numbers of atoms

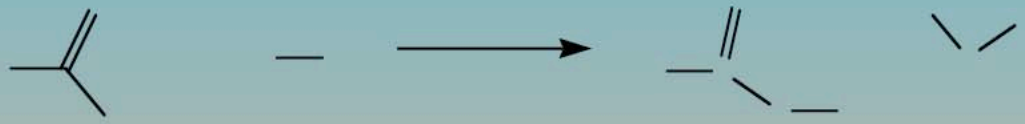
400	Carbon
322	Hydrogen
81	Oxygen

Numbers of functional groups

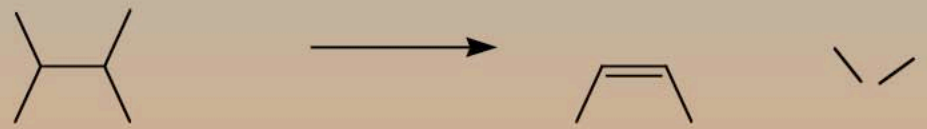
40	Total ring structures
40	Phenyl rings
1	Alcohol
1	Phenol
118	Ether linkages

Model reactions transform structure

Ester Hydrolysis 

Ester Condensation 

Amide Hydrolysis 

Dehydration 

Microbial uptake 

Reaction Probabilities: P calculated from

Molecular structure

Environment (pH, light intensity, etc.)

Proximity of near molecules

State (adsorbed, micellar, etc.)

Length of time step, _t

Example: Ester Hydrolysis

$$P = (\#\ \text{Esters})\ A\ e^{-Ea/RT}\ (1 + b[H^+] + c[OH^-])$$

Where A = Arrhenius constant

E_a = activation energy

R = gas constant

T = temperature, Kelvins

b = acid catalyzed pathway

c = base catalyzed pathway

Property prediction

Environmental

Light absorbance

Molecular weight

Acid content & pK_a

Bioavailability

K_{ow}

Metal binding K

Analytical

Elemental %

Titration curves

IR Spectra

NMR spectra

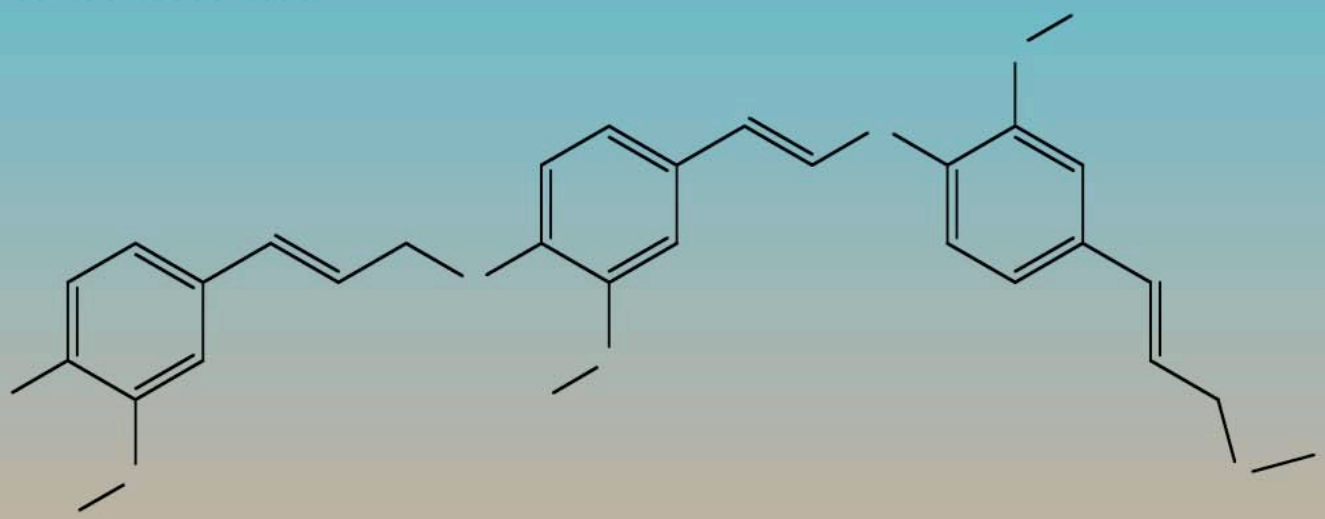
Property Calculation Methods

- Trivial- MW, elemental composition, Equivalent weight
- Simple QSAR- pK_a, K_{ow}
- Interesting
  - Bioavailability
  - Light absorption
  - Metal binding

Presentation and Analysis

- Spatial mapping of molecules
- Results stored in Oracle database
- Remote query via WWW interface
- Standard graphs of reaction frequency, molecular properties versus time

Trial: Can we convert lignin oligomer (MW ~6000) in "NOM" ?



Atmospheric O_2

Neutral pH

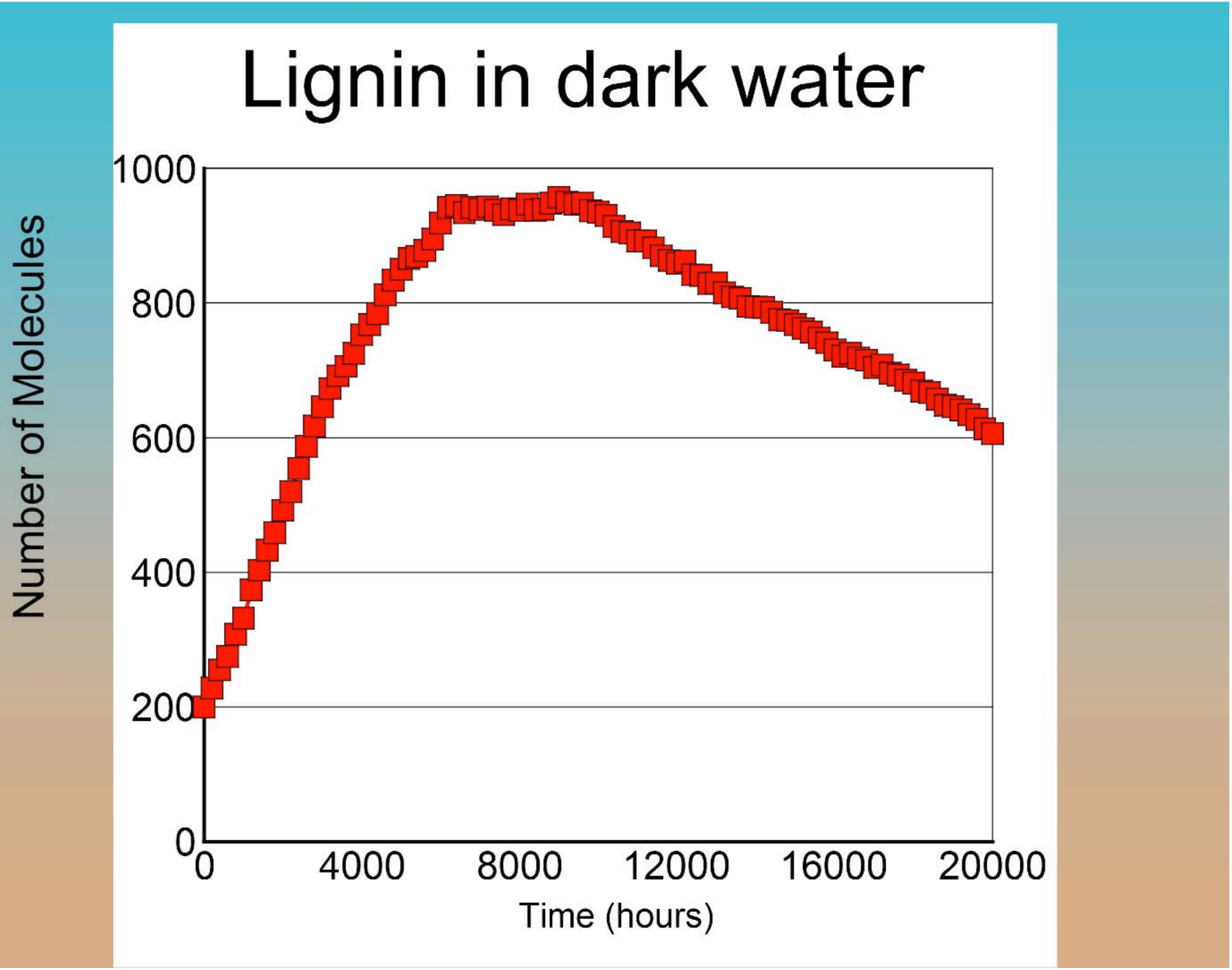
Moderate enzyme activity

27 months reaction time

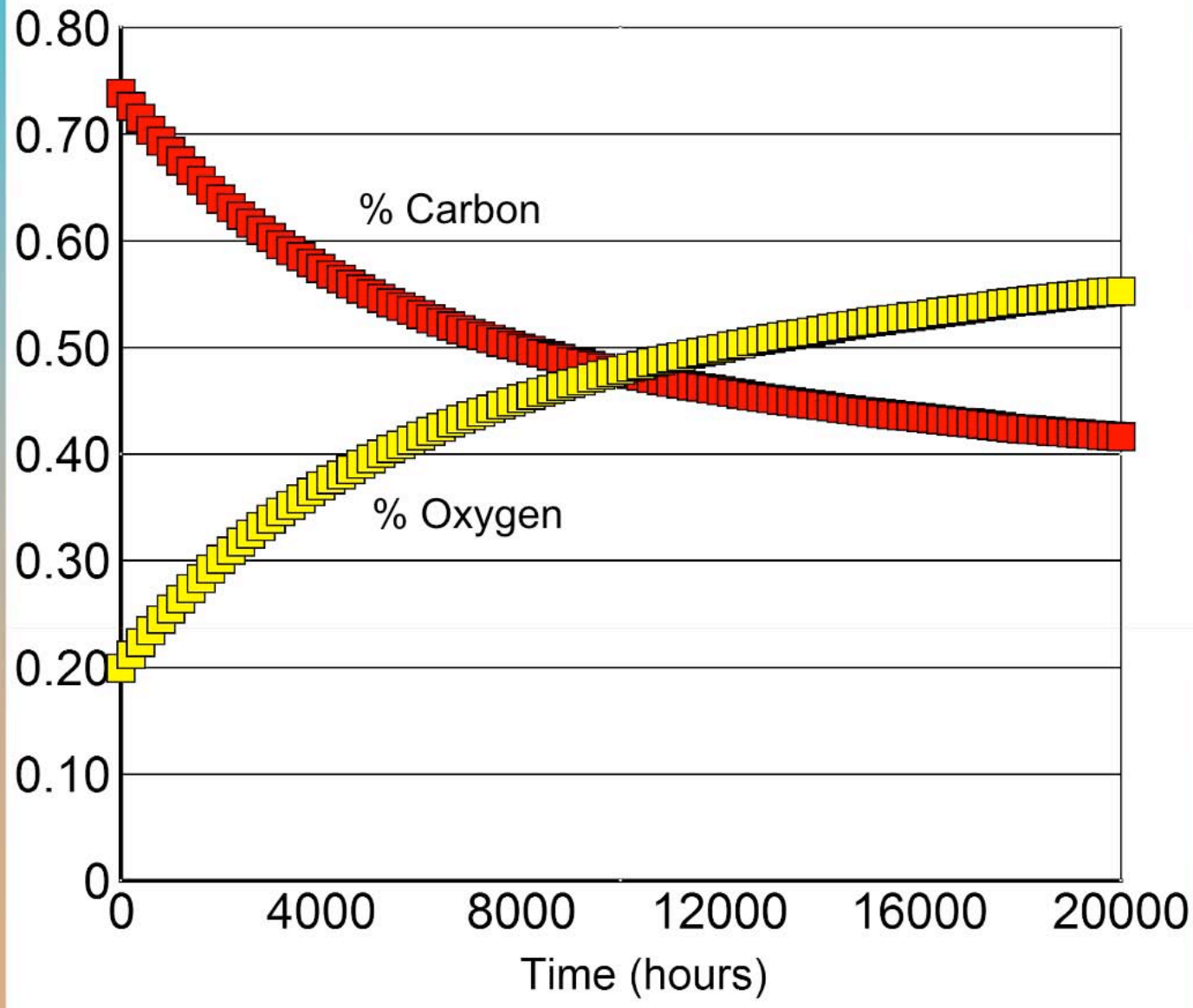
No light

No surfaces

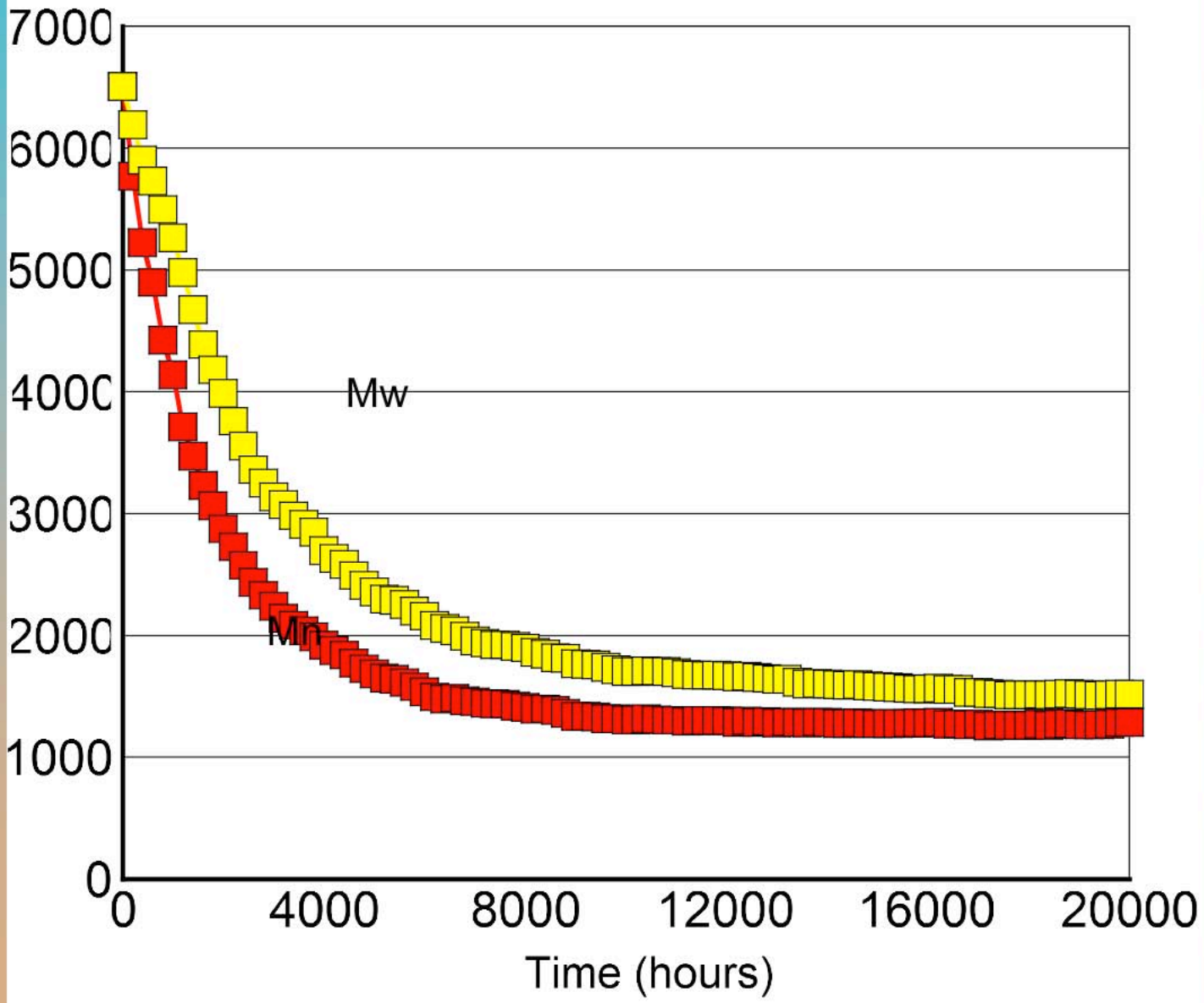
No transport


Lignin in dark water
Number of Molecules
1000
800
600
400
200
0
0
4000
8000
12000
16000
20000
Time (hours)

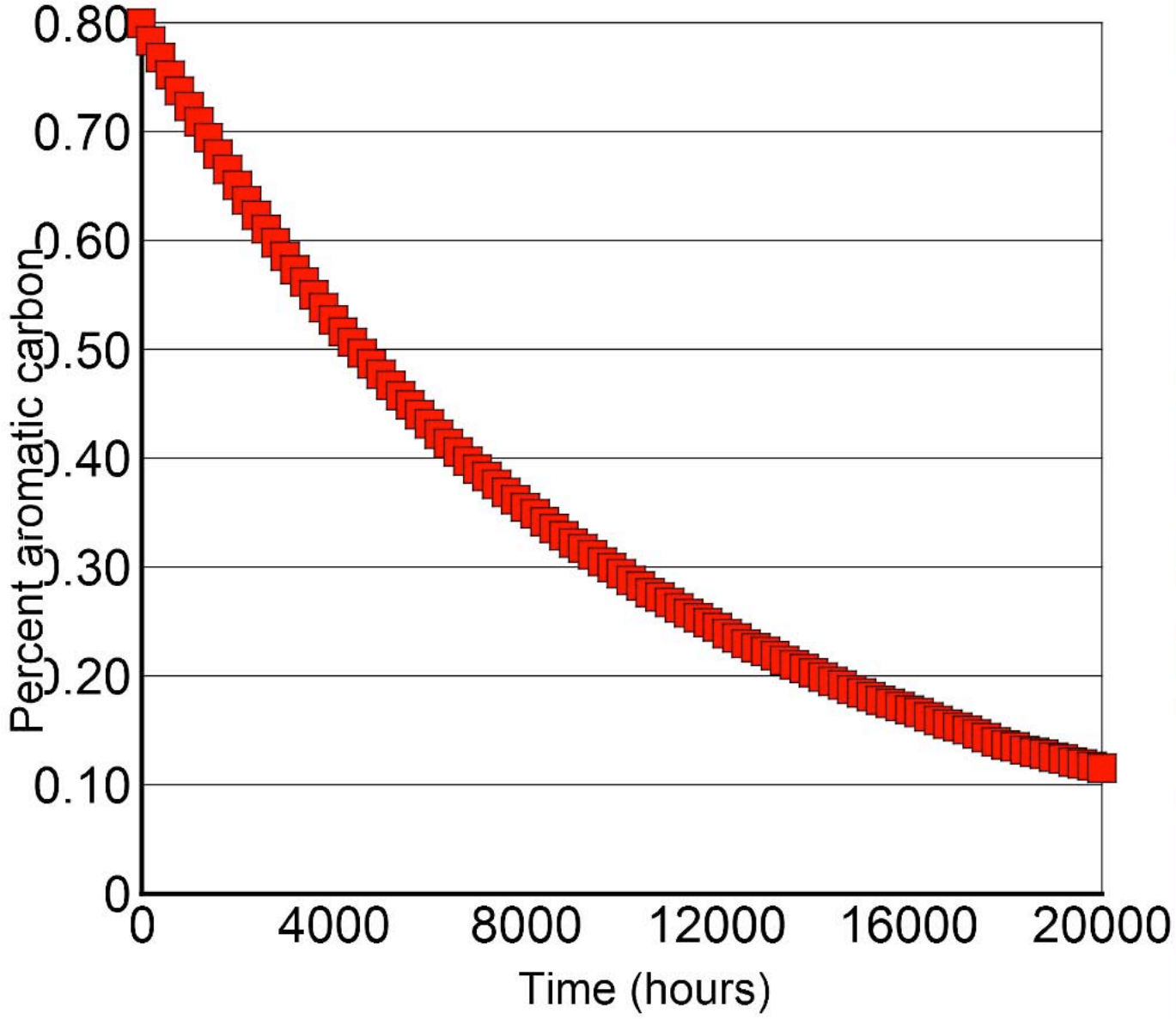
Lignin in dark water



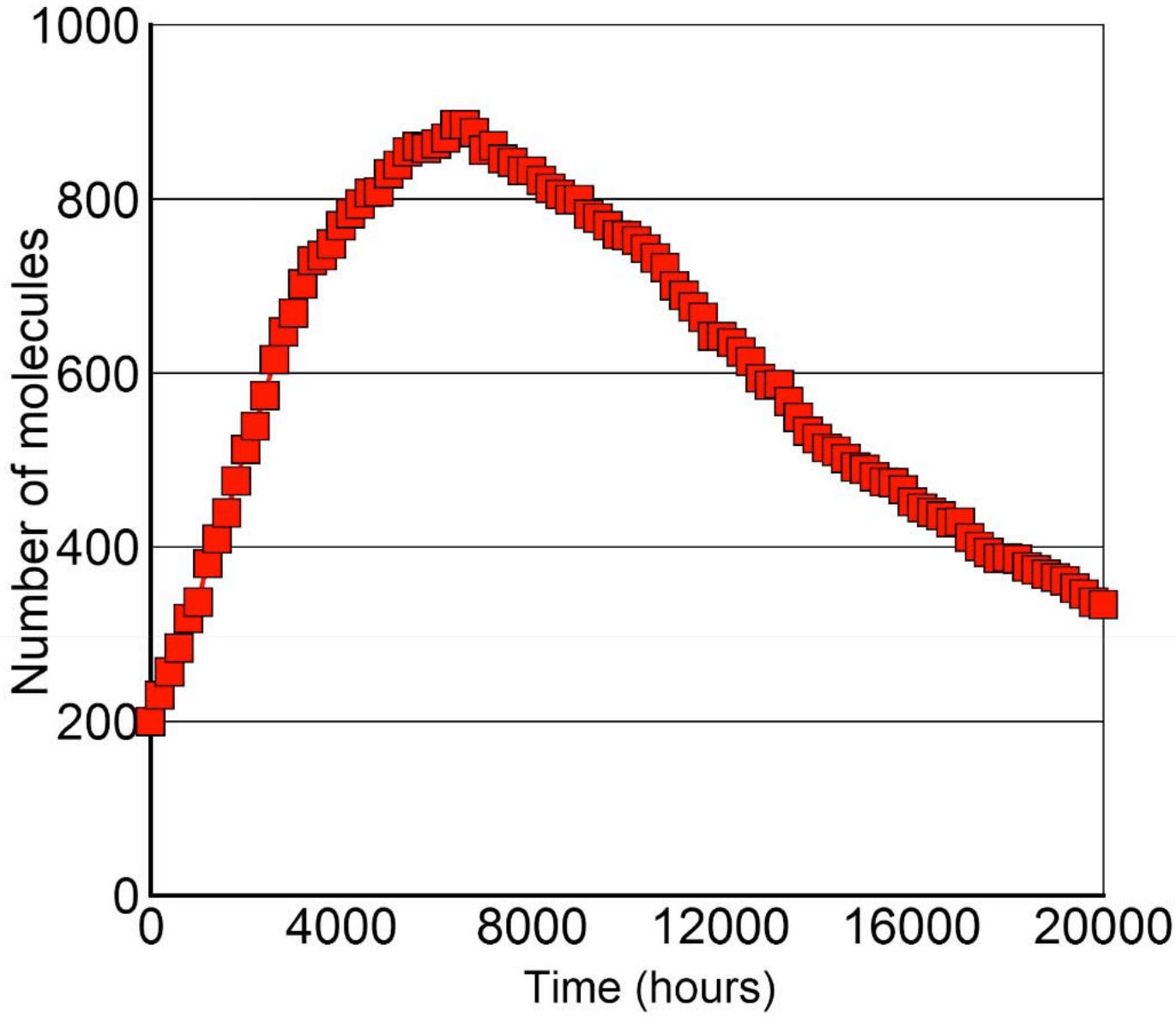
Lignin in dark water



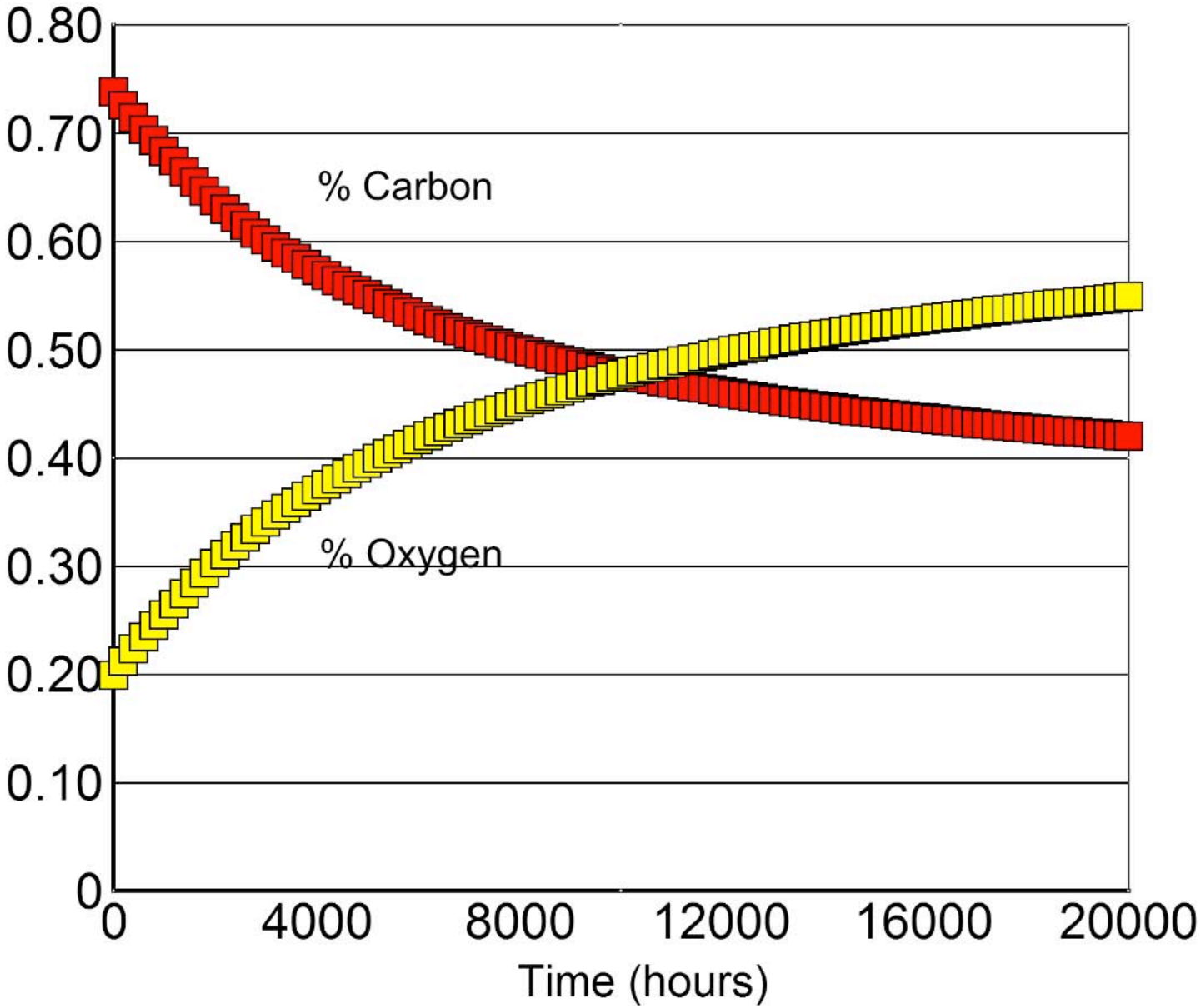
Lignin in dark water



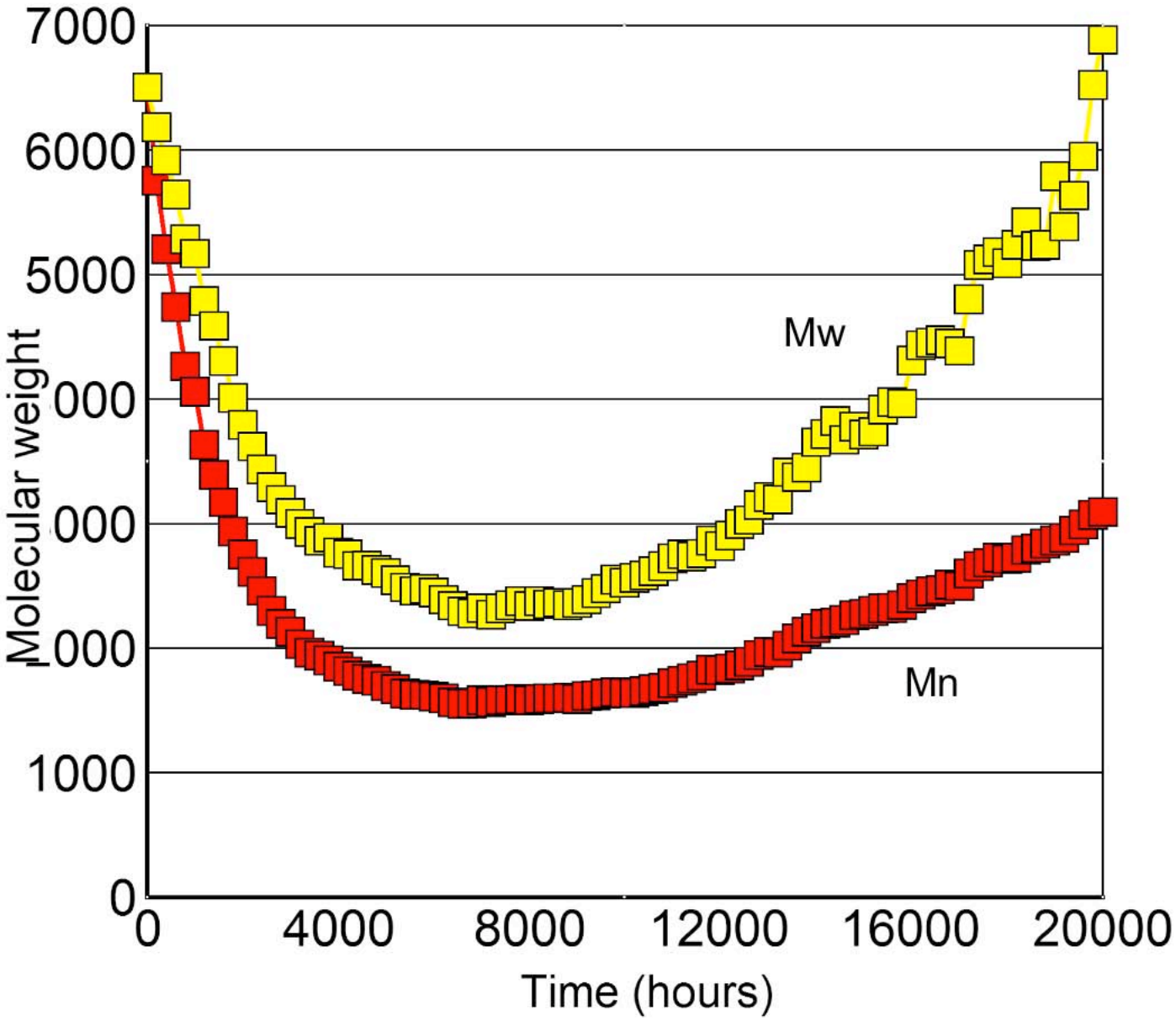
Lignin in dark, acidic soil



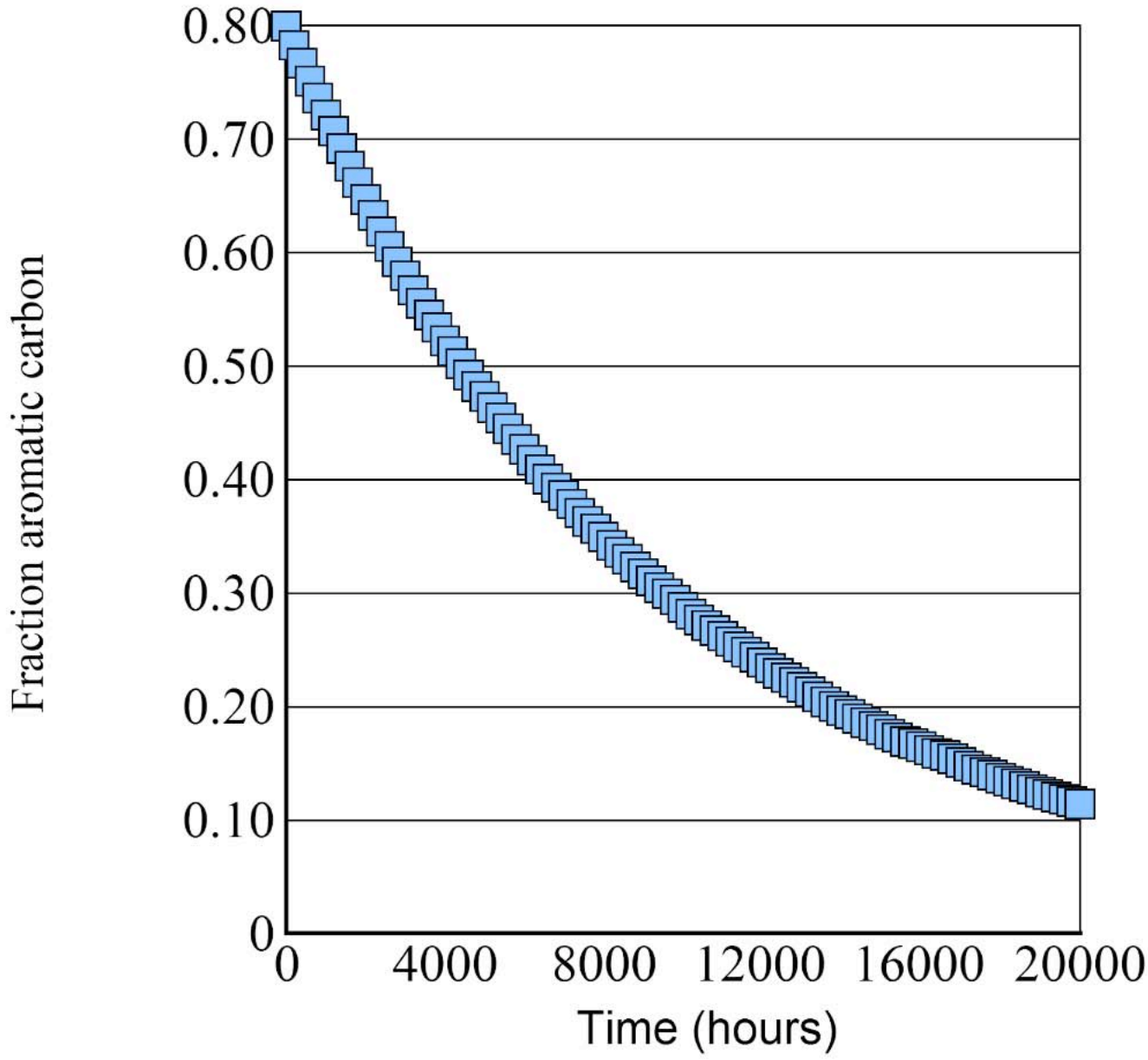
Lignin in dark, acidic soil



Lignin in dark, acidic soil



Lignin in dark, acidic soil



Lignin -> NOM conversion

- Elemental composition similar to whole water NOM
- Average MW within range for aquatic NOM, soil NOM respectively
- Aromaticity lower than normal

Stochastic synthesis
Preliminary tests

- Chromatography-like NOM movement in soils and sub-surface
- Log-normal distribution of NOM molecular weights
- Rapid consumption of proteins

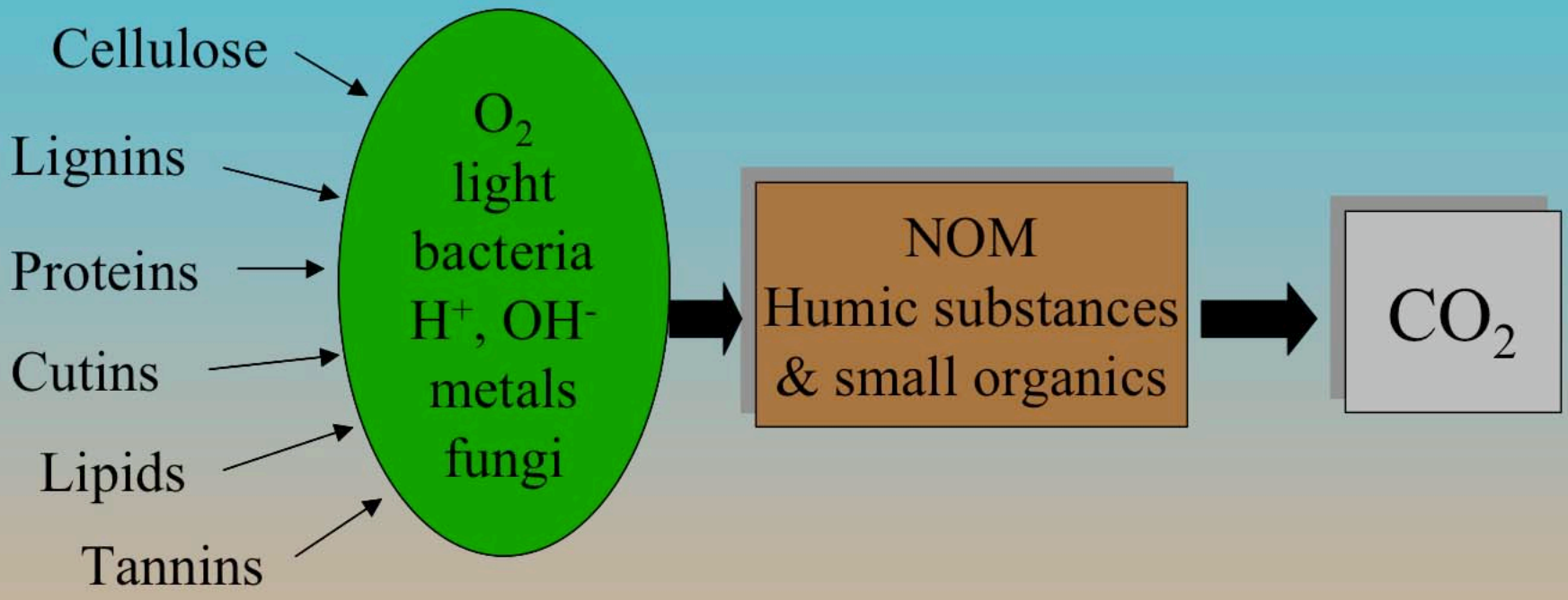
Current development

- Expanding reaction set
- Determination of reaction probabilities
- Best method of spatial mapping
  - Discrete grid vs Continuous space
- Remote query capability

Next Steps-

- Property prediction algorithms
- Data mining capabilities
- Comparison with lab and field results

Stochastic Synthesis of NOM



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

Financial Support

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Collaborating Scientists

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