# Plant Biochemical Shifts Under Varying Nitrogen Conditions: Implications for the Carbon Cycle

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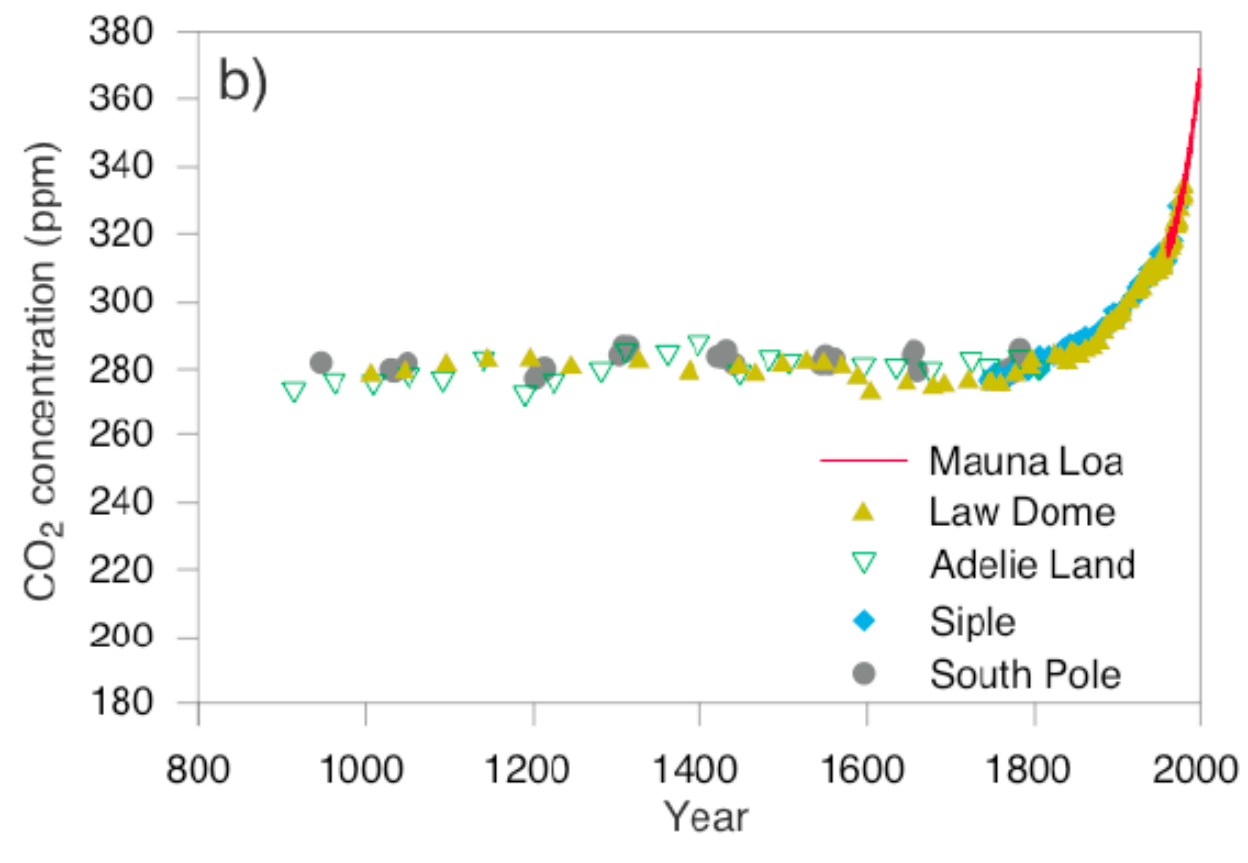
# Outline

- Background
  - Carbon Cycle
  - Carbon Oxidation State ($C_{ox}$) & Oxidative Ratio (OR)
- Site
  - Nitrogen Rate Experiment of a Corn Ecosystem in Michigan
- Methods
  - Elemental Analysis
  - $^{13}C$ Nuclear Magnetic Resonance Spectroscopy
- Results
  - Plant Biochemistry
  - $C_{ox}$ & OR
- Conclusions, Implications, & Future Works

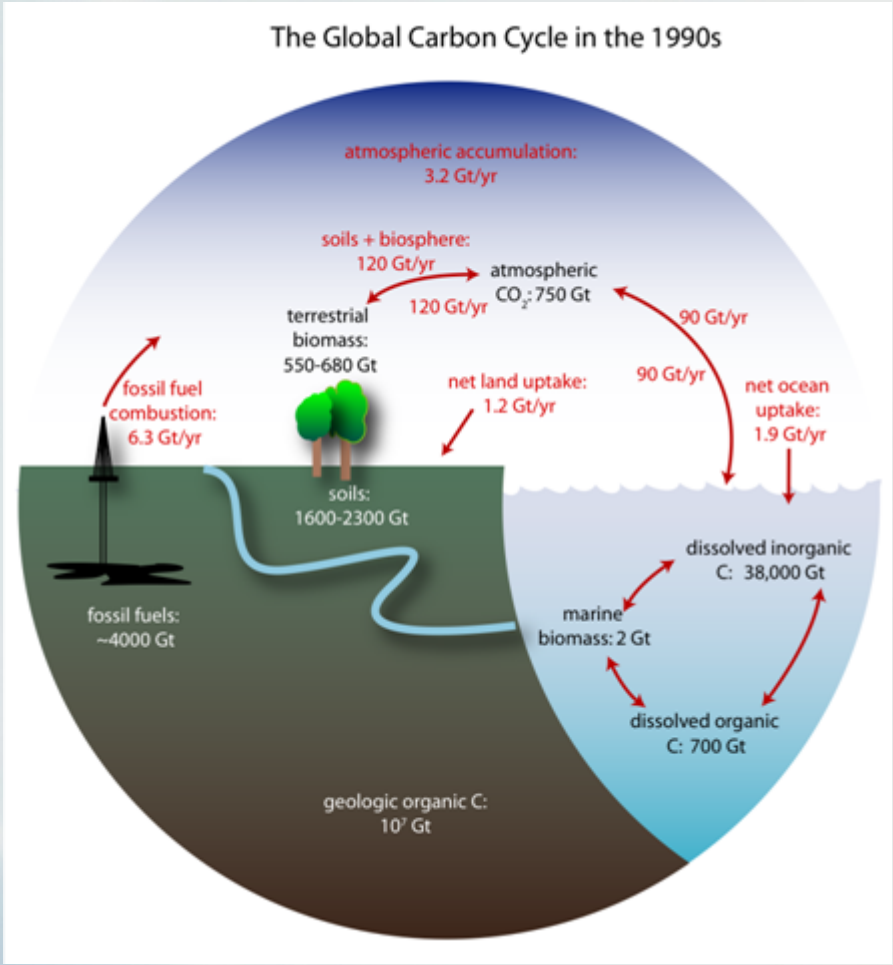
# Atmospheric $CO_2$ Concentrations are Increasing




Prentice et al. 2001

# Anthropogenic $CO_2$ Emissions Are Influencing the Global Carbon Cycle

- Fossil Fuel Combustion
  - 6.4 ± 0.4 Pg C/yr
- Atmospheric Accumulation
  - 3.2 ± 0.1 Pg C/yr

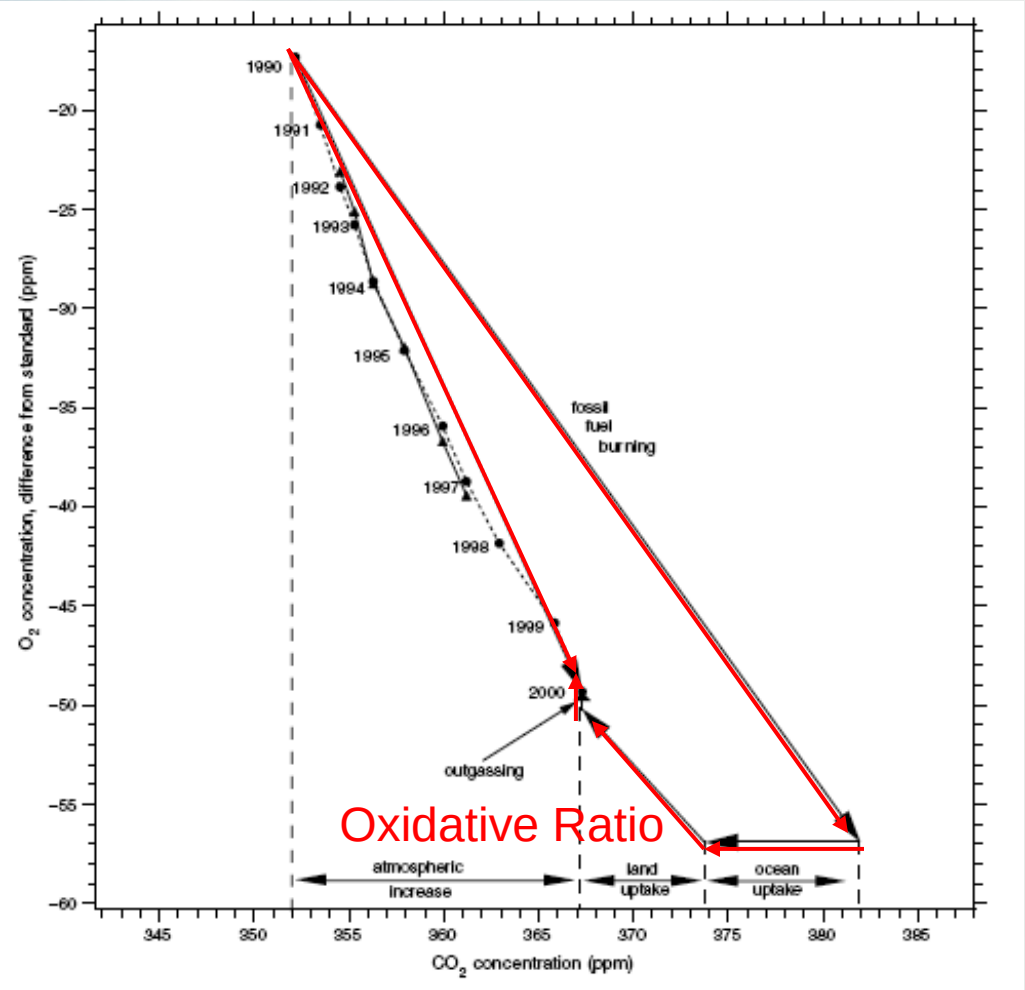



Adapted from Prentice et al. 2001
by C.A. Masiello

1 Gt C = 1 Pg C = $10^{15}$ g C

# Carbon Reservoir Apportionment

- Terrestrial biosphere draws down $CO_2$ while simultaneously releasing $O_2$ via photosynthesis
- Ocean draws down $CO_2$ via dissolution
- Small $O_2$ outgas from ocean




Climate Change 2001: The Scientific Basis

# Oxidative Ratio (OR)

$$OR = \frac{\text{moles } O_2}{\text{moles } CO_2}$$

Photosynthesis:

$$CO_2 + H_2O + NH_3 \rightarrow C_xH_yO_zN_w + O_2$$

$$OR = \frac{\text{moles } O_2 \text{ fixed}}{\text{mole } CO_2 \text{ consumed}}$$

Respiration/Decomposition:

$$C_xH_yO_zN_w + O_2 \rightarrow CO_2 + H_2O + NH_3$$

$$OR = \frac{\text{moles } O_2 \text{ consumed}}{\text{mole } CO_2 \text{ fixed}}$$

Randerson et al. 2006;
Masiello et al. in press 2008

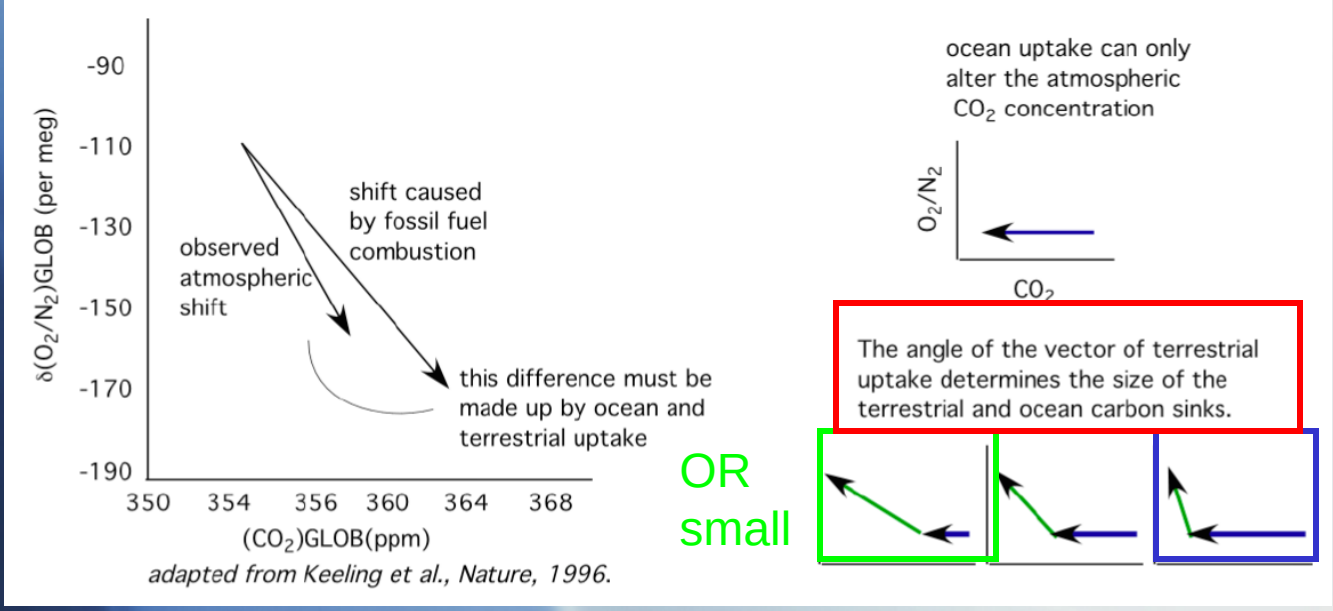
# OR & Apportionment

- Hypothesis:

  Ecosystem OR is not constant
- Can vary as a function of:
  - Land use
  - Ecosystem nutrient status
  - Climate

$\Delta OR = 0.01 \rightarrow 0.1$ Pg C

Randerson et al. 2006



# Measuring OR

- Difficult to directly measure via gas exchange studies (Seibt. et al. 2004)

- Can use carbon oxidation state ($C_{ox}$) measurements to estimate OR

N Source: $NH_3$

$$OR = 1 - \frac{C_{ox}}{4}$$

N Source: $HNO_3$

$$OR = 1 - \frac{C_{ox}}{4} + \frac{2N}{C}$$

# Carbon Oxidation State ($C_{ox}$)

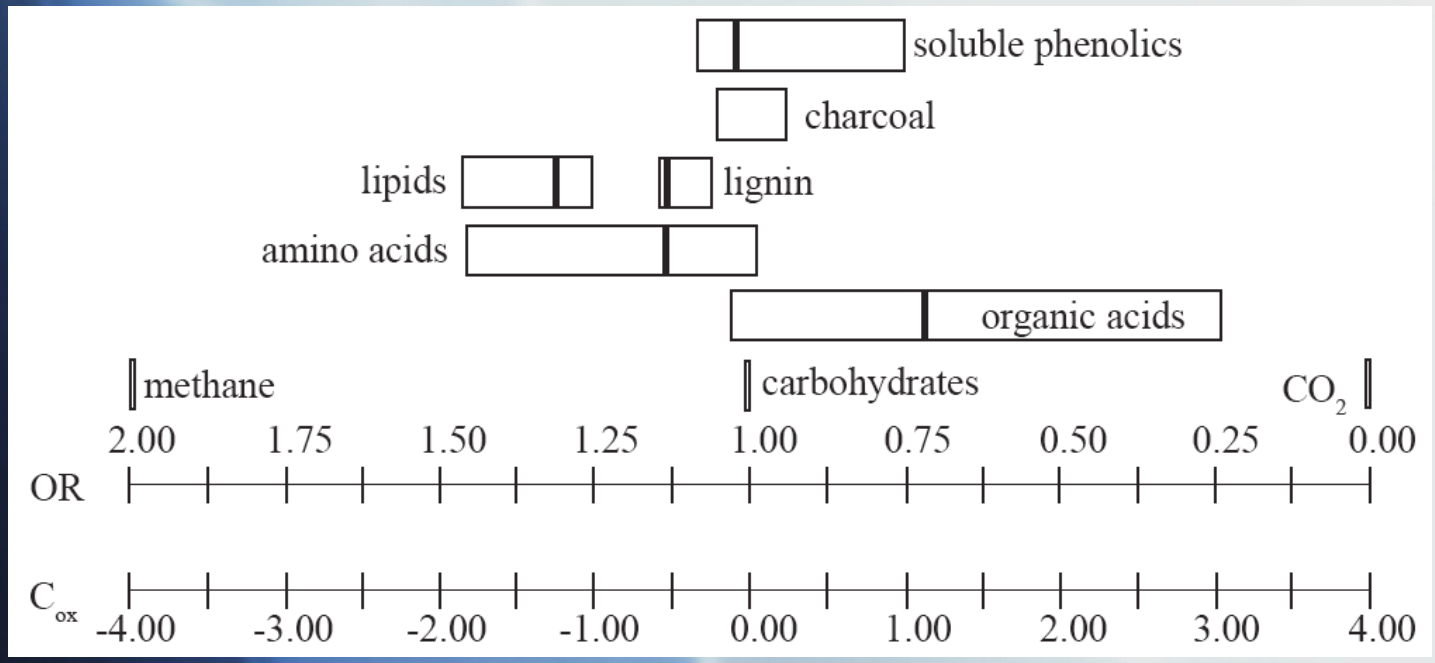
$$C_{ox} = \frac{2[O] - [H] + 3[N]}{[C]}$$

$H_{ox} = {}^{+}1$

$O_{ox} = {}^{-}2$

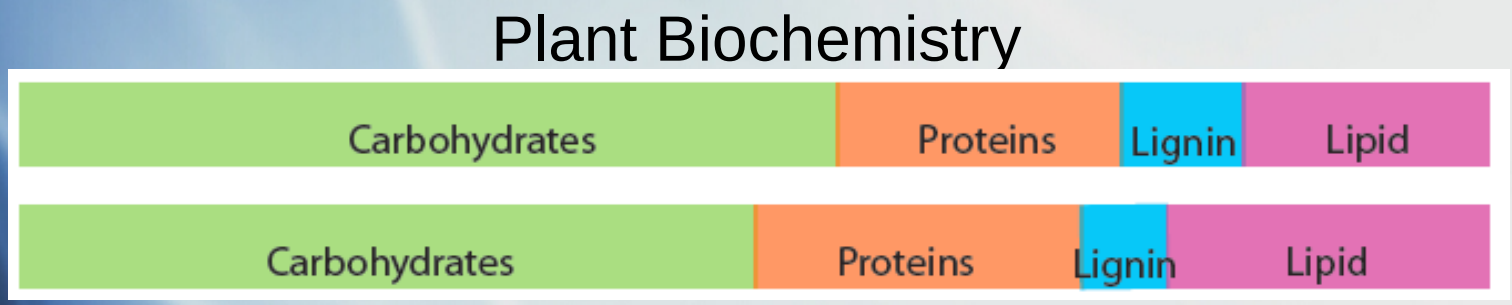
$N_{ox} = {}^{-}3$

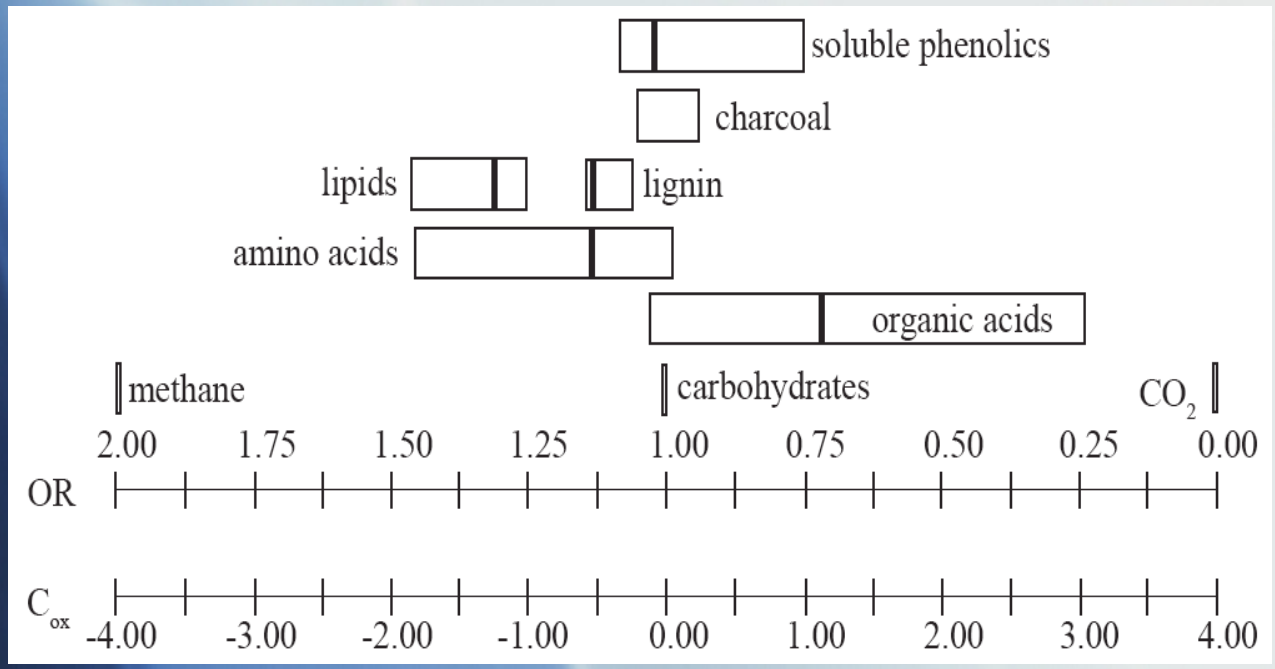
$C_xH_yO_zN_w$



# Plant Biochemical Composition

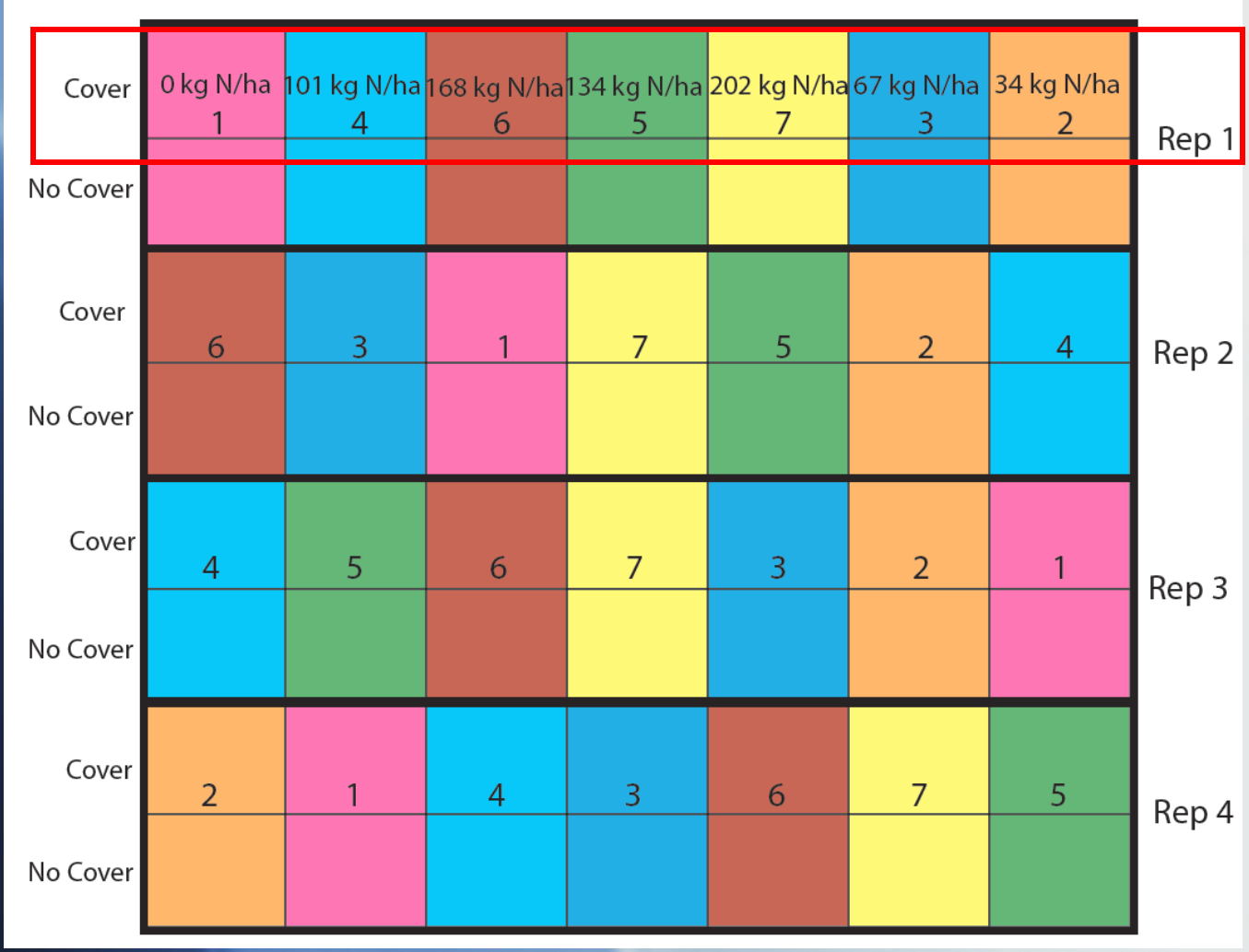
- Changes in the relative abundance of biomolecules within a plant can alter a plant's $C_{ox}$ & OR



# Site

- Kellogg Biological Station - Michigan
  - Nitrogen Rate Experiment on Corn Ecosystem




Numbers indicate fertilization rates

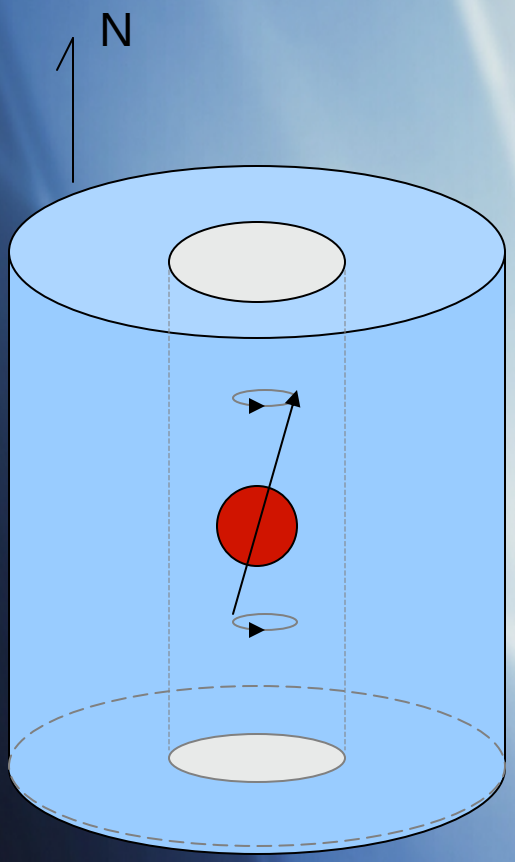
1-lowest;

7-highest

# Methods

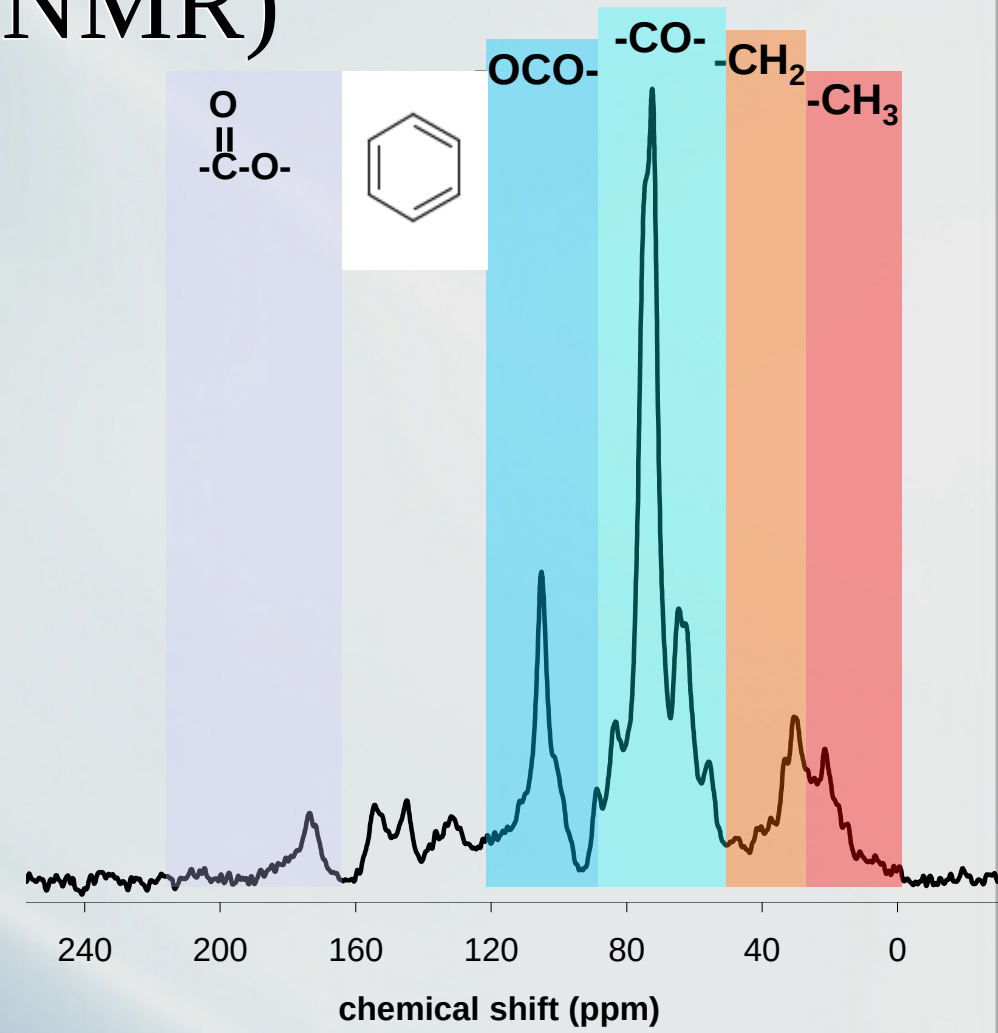

- Elemental Analysis
  - CosTech CHNSO Elemental Combustion System
    - %C & %N
- $^{13}C$ Nuclear Magnetic Resonance (NMR) Spectroscopy
  - Bruker 200 MHz NMR Spectrometer
    - Type of carbon bonds in a molecule

# $^{13}C$ Nuclear Magnetic Resonance ($^{13}C$ NMR)



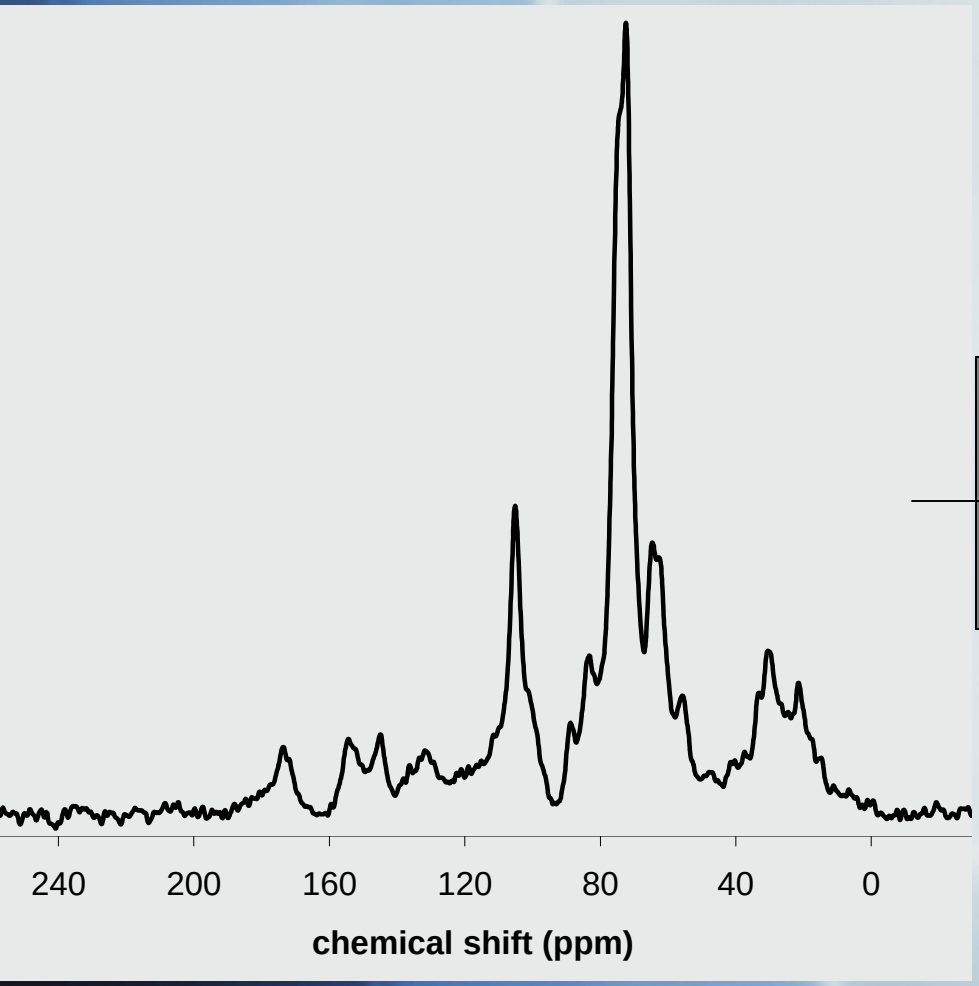

Cross Polarization/Magic Angle Spinning

Slide by WC Hockaday



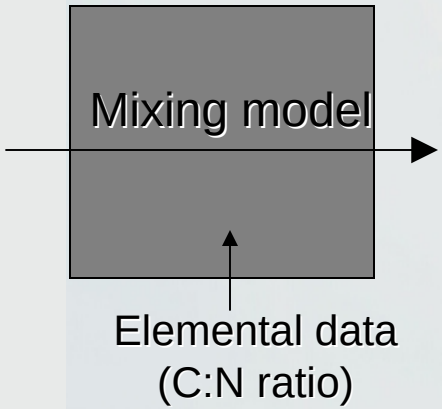

Resonance frequency

# Interpretation of $^{13}C$ NMR data




Resonance frequency

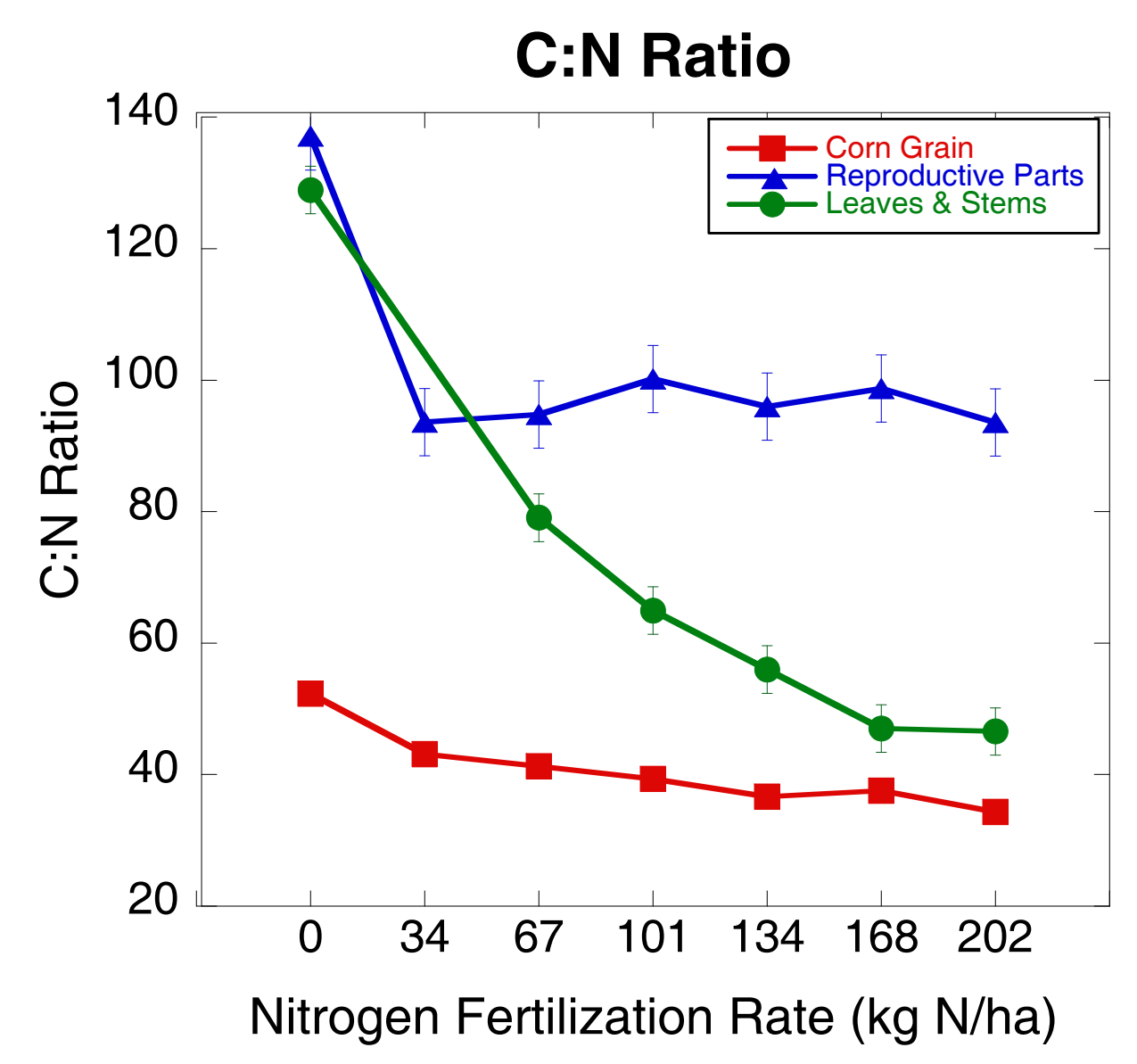
Nelson & Baldock 2005



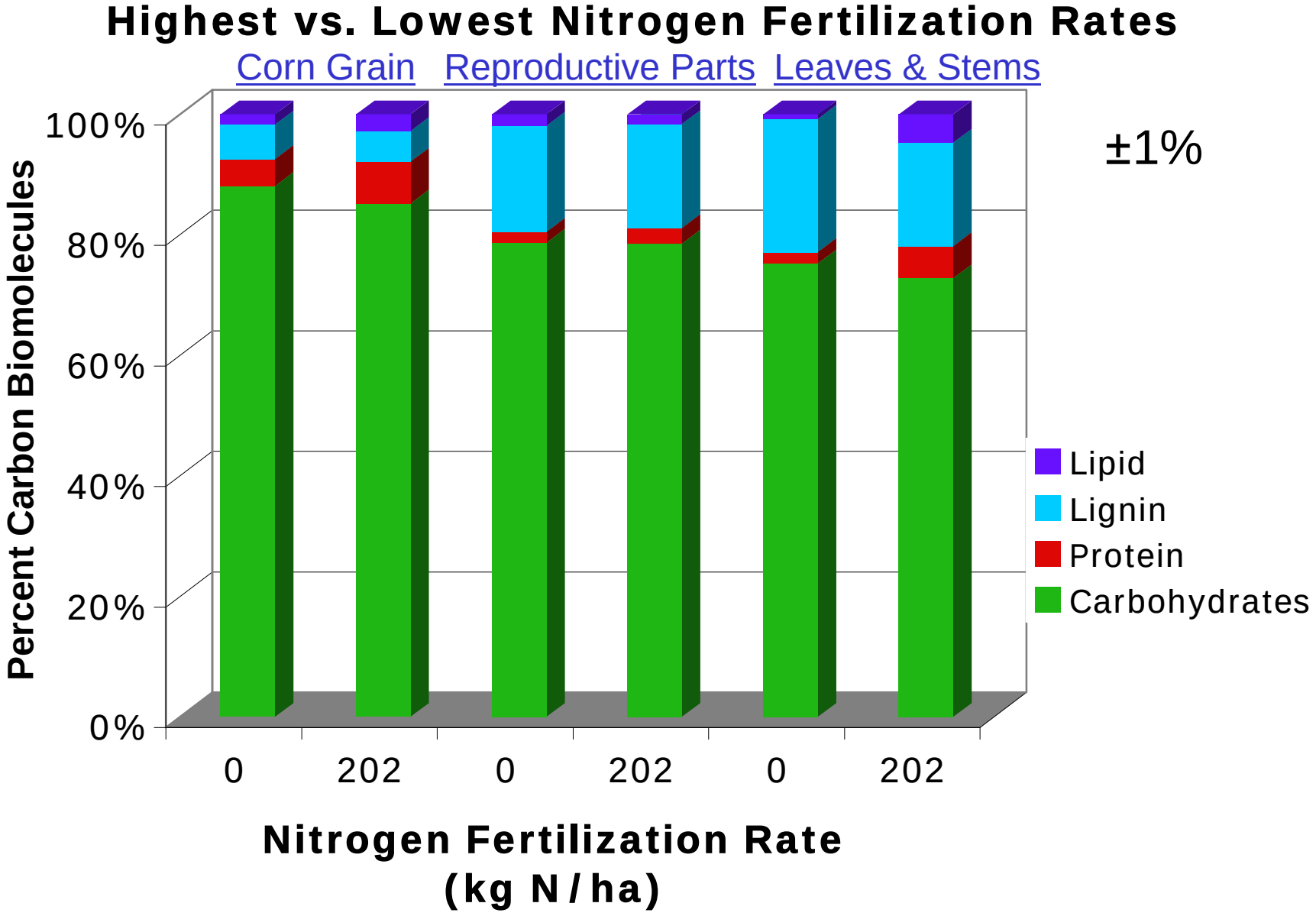

% Carbohydrate
% Lignin
% Lipid
% Protein

Slide by WC Hockaday

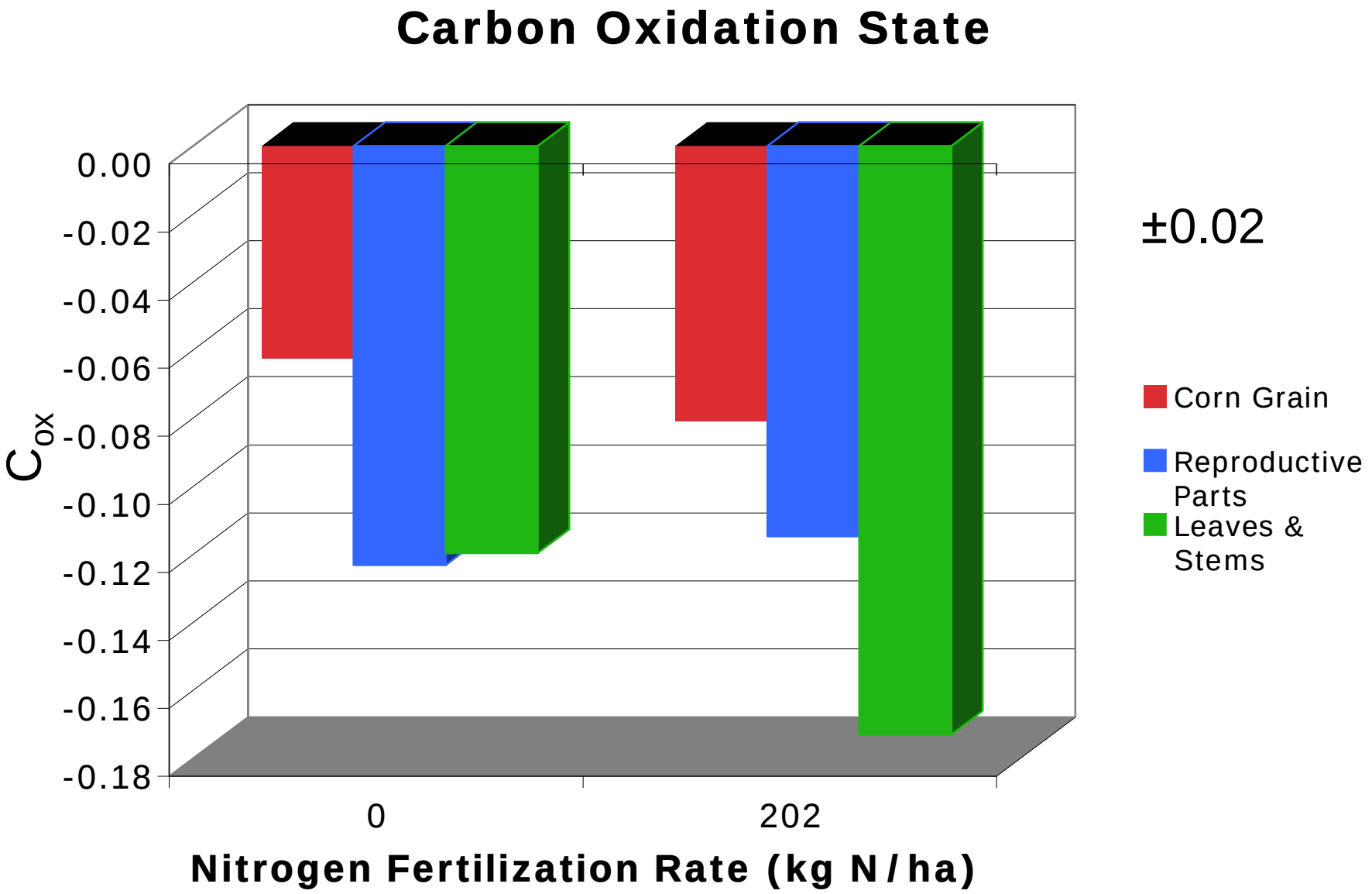
# C:N Ratio


C:N Ratio
Corn Grain
Reproductive Parts
Leaves & Stems
C:N Ratio
140
120
100
80
60
40
20
0
34
67
101
134
168
202
Nitrogen Fertilization Rate (kg N/ha)

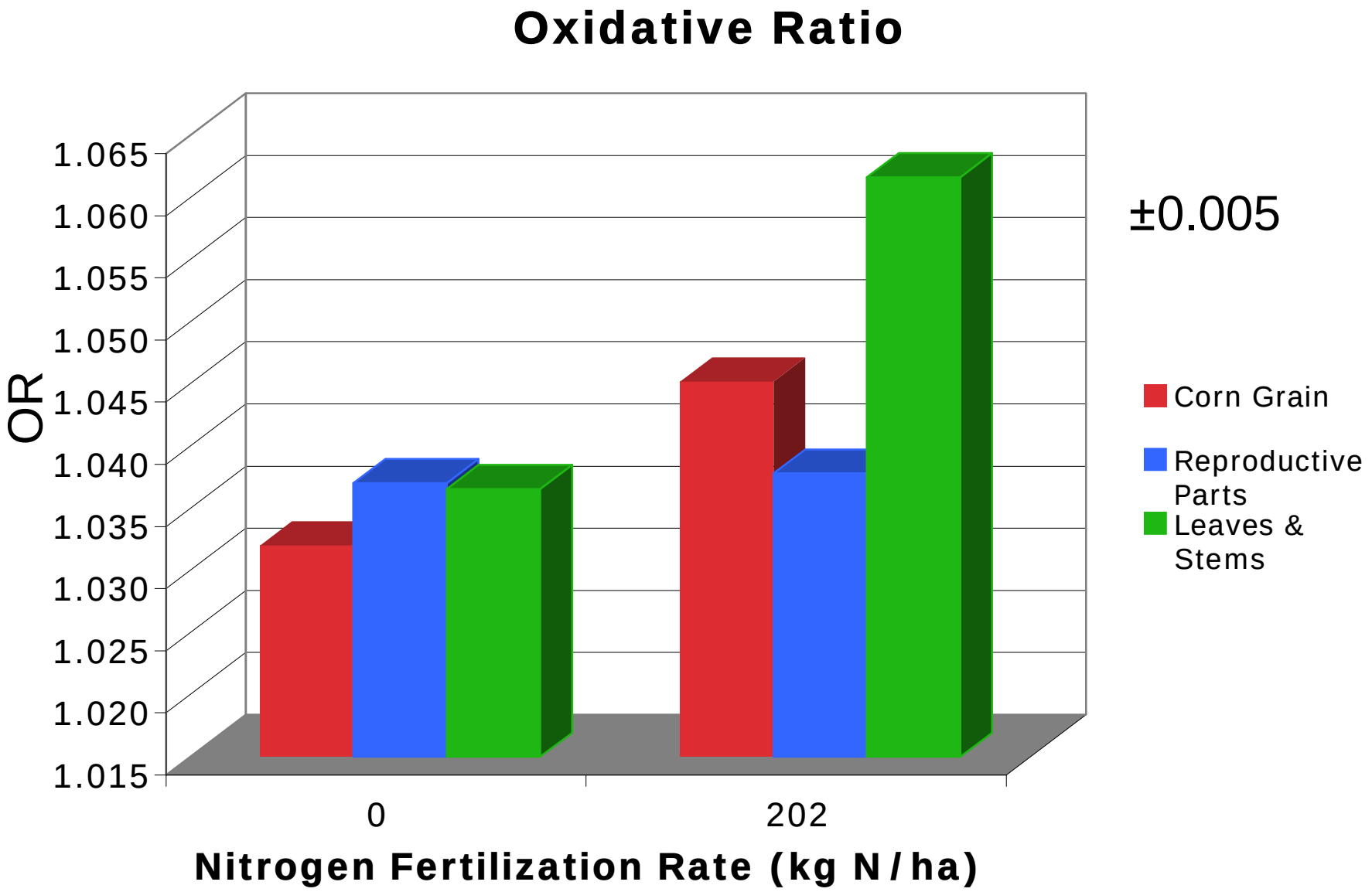
# Changes in Plant Biochemistry



# $C_{ox}$


Carbon Oxidation State
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
-0.18
Cox
0
202
Nitrogen Fertilization Rate (kg N/ha)
±0.02
Corn Grain
Reproductive Parts
Leaves & Stems

# OR


Oxidative Ratio
OR
1.065
1.060
1.055
1.050
1.045
1.040
1.035
1.030
1.025
1.020
1.015
0
202
Nitrogen Fertilization Rate (kg N/ha)
±0.005
Corn Grain
Reproductive Parts
Leaves & Stems

# Conclusion

- Plant Biochemistry
  - Carbohydrates: No change
  - Protein: Increase
  - Lignin: Decrease for Grain and Leaves & Stems
  - Lipids: Increase for Grain and Leaves & Stems; Decrease for Reproductive Parts
- $C_{ox}$: overall corn becomes more reduced
- OR increases as nitrogen supply increases

# Implications

- Changes in nitrogen supply to corn can:
  - Alter the quality of the grain which is used for feedstock & food
  - Alter the biochemistry of litter which can affect
    - Soil microbial community
    - Soil carbon pools
  - Alter ecosystem $C_{ox}$ & OR

# Future Work

- Collect data for more replicates
- Weight results with NPP data
- Measure $C_{ox}$ & OR via Elemental Analysis
  - Compare with that estimated from Mixing Model

# Acknowledgements


- Dr. Carrie Masiello
- Dr. Bill Hockaday
- The Kellogg Biological Station for providing samples from the N Rate Study, particularly Dr. Claire McSwiney & Dr. Phil Robertson
- Dr. Jeff Baldock for providing the NMR mixing model
- Funding: NSF DEB 0614524 & NSF DEB 0445282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Questions?

**Thank You!!!**

# Mixing Model

components $a + b + c + d + e + f = 1$

N:C ratio $a(n_A) + b(n_B) + c(n_C) + d(n_D) + e(n_E) + f(n_F) = n_{sample}$

45-10 ppm $a(\alpha_A) + b(\alpha_B) + c(\alpha_C) + d(\alpha_D) + e(\alpha_E) + f(\alpha_F) = \alpha_{sample}$

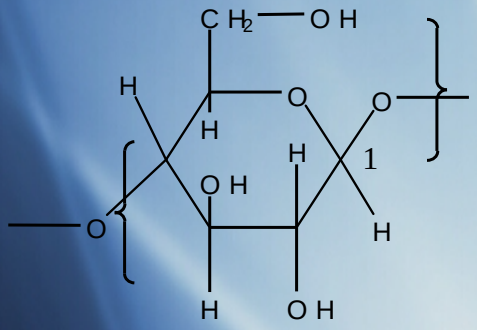
95-60 ppm $a(\beta_A) + b(\beta_B) + c(\beta_C) + d(\beta_D) + e(\beta_E) + f(\beta_F) = \beta_{sample}$

210-165 ppm $a(\chi_A) + b(\chi_B) + c(\chi_C) + d(\chi_D) + e(\chi_E) + f(\chi_F) = \chi_{sample}$

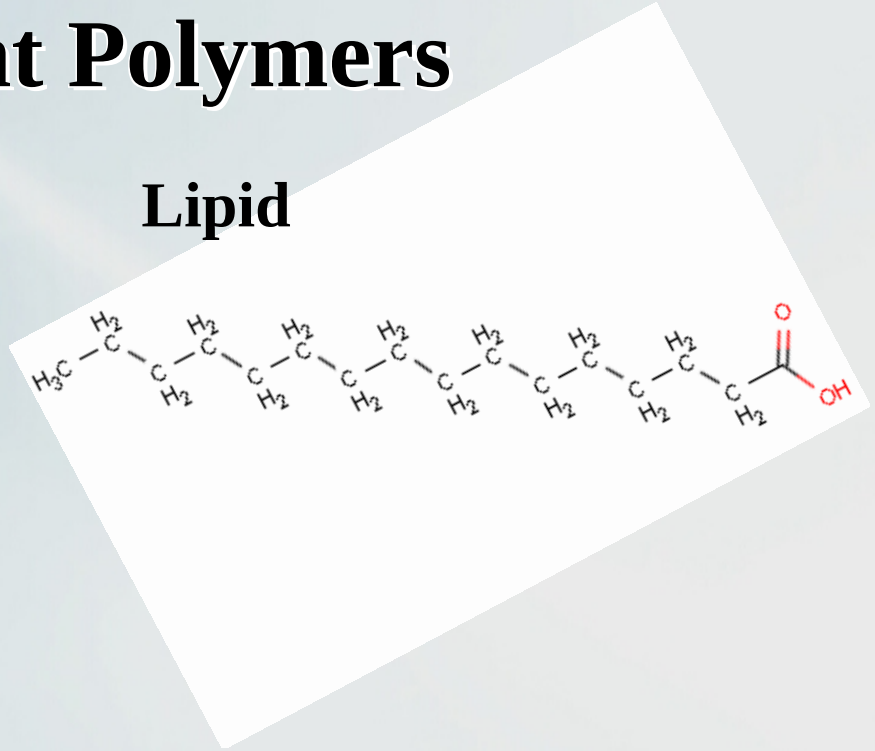
145-110 ppm $a(\delta_A) + b(\delta_B) + c(\delta_C) + d(\delta_D) + e(\delta_E) + f(\delta_F) = \delta_{sample}$

# Plant Polymers

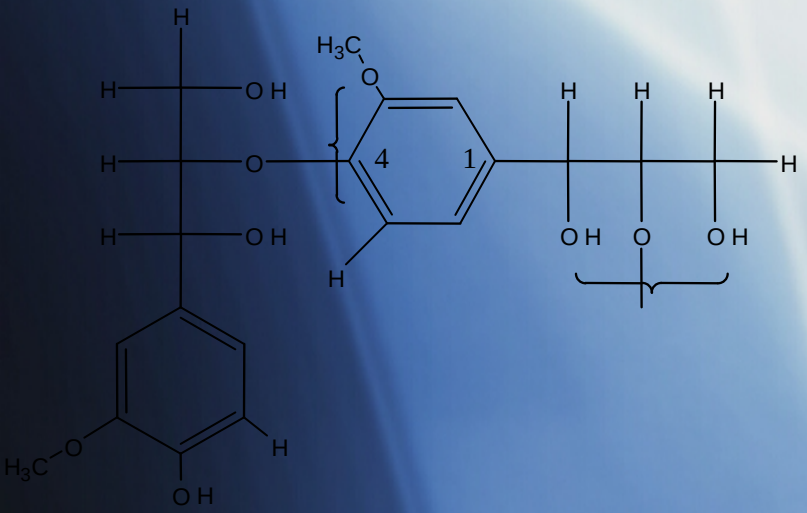
## Cellulose



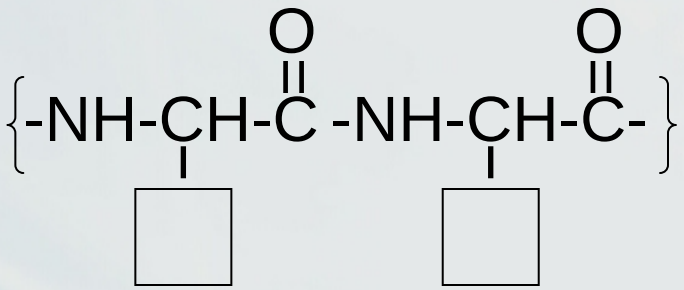
## Lipid



## Lignin



## Protein



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