Outline

• The Problem of Too Much Bioavailable Carbon
• Production and Characterization of Fast Pyrolysis Biochars
• Incubation Study
• Carbon Mineralization Rates
• Soil Properties
• Microbial Populations
BIOAVAILABLE = ABLE TO BE METABOLIZED

Metabolized to CO₂, especially by microorganisms.
Too Much Bioavailable Carbon

- Soil microorganisms will consume any bioavailable carbon
- Growth requires carbon and nitrogen
- If the C:N ratio is too high, microbes will scavenge the area for nitrogen, leaving too little for plants

CS = corn stover; CCS = carbonized corn stover

Photo from Steiner, et. al, The Influence of Crop Residues and Carbonized Crop Residues on Nitrogen Dynamics, North American Biochar 2009 Conference
BIOAVAILABLE CARBON IS NOT SEQUESTERED CARBON
Fast Pyrolysis

• Optimized for bio-oil production
  – Moderate temperatures (400-600°C)
  – Very fast heating rate (~1000°C/s)
  – Short residence times (<2s)
• Products are ~70% bio-oil, 15% char and 15% non-condensable gases
• Concern that fast pyrolysis biochars contain too much bioavailable carbon
  – Condensed bio-oil vapors
  – Insufficient reaction times
## Production of Biochars

Incompletely pyrolyzed chars

<table>
<thead>
<tr>
<th>Biochar</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>Corn Stover</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor</td>
<td>Fluidized Bed</td>
<td>Freefall</td>
<td>Freefall</td>
</tr>
<tr>
<td><strong>Reactor Temp.</strong></td>
<td>500°C</td>
<td>500°C</td>
<td>600°C</td>
</tr>
<tr>
<td>Feed Rate</td>
<td>5 kg/hr</td>
<td>0.5 kg/hr</td>
<td></td>
</tr>
<tr>
<td>Particle Size</td>
<td>&lt;6 mm</td>
<td>500 µm</td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>2%</td>
<td>3%</td>
<td>2%</td>
</tr>
<tr>
<td>Volatiles</td>
<td>14%</td>
<td>26%</td>
<td>17%</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>25%</td>
<td>35%</td>
<td>31%</td>
</tr>
<tr>
<td>Ash</td>
<td>59%</td>
<td>46%</td>
<td>56%</td>
</tr>
<tr>
<td>Elemental C</td>
<td>30%</td>
<td>35%</td>
<td>31%</td>
</tr>
<tr>
<td>C:N Ratio</td>
<td>46</td>
<td>51</td>
<td>54</td>
</tr>
</tbody>
</table>
Biochar Characterization

Qualitative CP/MAS/TOSS $^{13}$C NMR spectra of corn stover and corn stover biochars
Biochar Characterization

Quantitative DP/MAS 13C NMR spectra of corn stover and corn stover biochars showing all carbon and non-protonated carbons (Cq).

ssb = spinning side bands
Incubation Study

- Soil: Sparta loamy fine sand
  - (87% sand, 9% silt, 4% clay)
- 0.5 wt % Amendment
  - Corn stover, Biochar 1, Biochar 2, Biochar 3
- N, P, S nutrient solution to 10% moisture
- Incubate in the dark at 23°C for 24 weeks
  - Soil sampling at week 8
- 9 replicates
Incubation Study

- \( \text{CO}_2 \) evolution measured by alkali trap
- Base neutralization quantified by acid titration
Carbon Mineralization Rates

Rate of evolution (mg CO₂-C/100g soil * day) vs. Incubation time (days)

- **Stover**
- **Biochar 2**
- **Biochar 3**
- **Biochar 1**
- **Control**
Readily Bioavailable Carbon

![Graph showing carbon evolution over time for different materials](graph.png)

- **Stover**
- **Biochar 2**
- **Biochar 3**
- **Biochar 1**

Amendment C evolved as CO$_2$ (wt % carbon added/jar) vs. Incubation time (days)
Carbon Mineralization Kinetics

\[ y = -0.00602x + 2.26 \quad R^2 = 0.968 \]
\[ y = -0.00023x + 2.16 \quad R^2 = 0.983 \]
\[ y = -0.00041x + 2.22 \quad R^2 = 0.995 \]
\[ y = -0.00042x + 2.18 \quad R^2 = 0.983 \]
\[ y = -0.00055x + 2.10 \quad R^2 = 0.994 \]
Soil Properties

**Soil Organic Matter**

<table>
<thead>
<tr>
<th></th>
<th>Char 3</th>
<th>Char 1</th>
<th>Stover</th>
<th>Char 2</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Matter (wt %)</td>
<td>2.0</td>
<td>1.9</td>
<td>1.9</td>
<td>1.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Total Nitrogen**

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>Char 3</th>
<th>Char 2</th>
<th>Char 1</th>
<th>Stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total N (wt %)</td>
<td>0.14</td>
<td>0.13</td>
<td>0.12</td>
<td>0.11</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**Soil pH**

<table>
<thead>
<tr>
<th></th>
<th>Char 1</th>
<th>Char 2</th>
<th>Stover</th>
<th>Char 3</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (1:5 in water)</td>
<td>6.1</td>
<td>6.0</td>
<td>5.9</td>
<td>5.8</td>
<td>5.7</td>
</tr>
</tbody>
</table>

**Phosphorus**

<table>
<thead>
<tr>
<th></th>
<th>Char 2</th>
<th>Char 3</th>
<th>Char 1</th>
<th>Control</th>
<th>Stover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bray P (mg/kg)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>
Soil Properties

**Nitrate-N**

Soil NO$_3$-N (mg/kg)

- Control
- Char 2
- Char 3
- Char 1
- Stover

**Ammonium-N**

Soil NH$_4$-N (mg/kg)

- Control
- Char 1
- Stover
- Char 2
- Char 3

**Potassium**

Available K (mg/kg)

- Char 2
- Char 3
- Char 1
- Stover
- Control

**Calcium**

Available Ca (mg/kg)

- Char 1
- Char 2
- Stover
- Char 3
- Control
Water Retention Capacity

Soil moisture (% soil dry weight)

Tension pressure (kPa)

- 33 kPa
- 500 kPa

- Stover
- Biochar 1
- Biochar 2
- Biochar 3
- Control

**Legend:**
- a
- ab
- abc
- bc
Microbial Populations

**Bacteria & Actinomycetes**

<table>
<thead>
<tr>
<th></th>
<th>Population (organisms/g dry soil)</th>
<th>Stover</th>
<th>Control</th>
<th>Char 2</th>
<th>Char 3</th>
<th>Char 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bacteria</td>
<td>[Bars showing population levels]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actinomycetes</td>
<td>[Bars showing population levels]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fungi**

<table>
<thead>
<tr>
<th></th>
<th>Population (organisms/g dry soil)</th>
<th>Stover</th>
<th>Char 1</th>
<th>Char 3</th>
<th>Control</th>
<th>Char 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Bar showing population levels]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Stover Control Char 2 Char 3 Char 1
- Bacteria & Actinomycetes
- Fungi

Note: The bars are labeled with letters (a, b) indicating statistical significance.
Conclusions

• The relative degree of pyrolysis completeness can be observed by several characterization methods, especially NMR

• A decreasing trend in amount of bioavailable carbon with increasing reaction completeness can be seen
Conclusions

• The relationships between biochar characteristics, carbon bioavailability and CO$_2$ respiration kinetics are complicated
  – Multiple types of carbon in biomass and biochars, each with its own decay kinetics
  – Soil organic matter oxidation and microbial metabolism convolute source of CO$_2$ emissions
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Questions?