Quantification of Biochar Soil Amendment by Near-Infrared Reflectance Spectroscopy

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Biochar

- Biochar is derived from organic materials through pyrolysis
- Pyrolysis is an anoxic thermochemical process (350°C-600°C) rendering:
  - Biochar
  - Bio-oil
  - Syngas (Biogas-separated or fed back)
Biochar

- Biochar used as a soil amendment
- Improves quality (BD, pH, CEC)
- Reduces leaching of nutrients
- Sequesters carbon

(Terra Preta – biochar treated Oxisol)
Biochar

- Potential C sequestration tool
- Possibility of C offset payments by Gov’t
- Need for measuring biochar applications to soil
- Current char-C analysis expensive and hazardous (use of high energy UV, HF and $^{13}$C-NMR)
Carbon forms in the soil

- Inorganic
  - mineral carbonates

- Organic
  - living biomass and fresh residue
  - particulate (resistant plant materials)
  - humus
  - black carbon (charcoal, soot)
NIRS theory

- Near Infrared Reflectance Spectroscopy (diffuse reflectance)
- Measures absorbance of radiation by measuring reflection
- Wavelength range of 400-2500 nm
- C-H, N-H, and O-H bonds stretch/bend
- Materials absorb NIR radiation proportional to compositional concentrations
NIRS applications

- Commercial and research grain/forage/feed/soil (composition/quality)
- Industrial process control in chemical/pharmaceutical (purity)
- Medical (hemoglobin)
- Remote sensing (plants & soils)
- Material science (optical communications)
- Astronomical (star age)
Review of Literature

NIR success in predicting soil C organic/inorganic fractions

(Chang et al., 2001; Chang and Laird, 2002; Brown et al., 2006)

...plus N, pH, Ca, Mg, moisture, CEC, texture
Review of Literature

★ MIR success in predicting soil C organic/inorganic fractions

★ MIR success in predicting soil C particulate/char fractions
  (Janik et al., 2007)

...plus N, pH, Ca, Mg, moisture, CEC, texture
  (Madari et al., 2006; Rossel et al. 2009)
Knowledge Gap

Can NIR be used to quantify char-C in soil?

(Bellon-Maurel and McBratney, 2011; Reeves, 2010)
Hypotheses

- **H0a**: NIRS cannot quantify the level of biochar in the soil.

- **H0b**: NIRS cannot distinguish between biochar C and other carbon contributions in the soil.

- **H1a**: NIRS has the ability to quantify the amount of biochar amendment the soil has received.

- **H1b**: NIRS can distinguish between biochar C and other carbon contributions in the soil.
Objectives

- Test the ability of NIRS to quantify biochar C
- Test the ability of NIRS to distinguish between biochar C and other carbon contributions in the soil
Experimental Design

- 2 Independent sets of samples
  - Column study
  - Field study

Each set served both as calibration and validation.
Experimental Design

Column Study

- Samples from ISU Agronomy Agricultural Engineering Research Center (AAERC)

- “Impact of biochar amendments on the quality of a typical Midwestern agricultural soil” (Laird et al., 2010a,b)

- 4 biochar levels, 2 manure trts, 6 reps, sampled at 3 depths = 144 samples

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Column N=144</th>
<th>Field N=216</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control TRT0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TRT1</td>
<td>5</td>
<td>6987.84</td>
</tr>
<tr>
<td>TRT2</td>
<td>10</td>
<td>13184.6</td>
</tr>
<tr>
<td>TRT3</td>
<td>20</td>
<td>-</td>
</tr>
</tbody>
</table>
Experimental Design

Field Study

- Samples from ISU Agronomy Agricultural Engineering Research Center (AAERC)

- Wider spatial variation than column set

- **3 biochar levels**, 3 residue rates, 4 reps, 6 samples per plot = 216 samples
Experimental Design

- Soil Sample Preparation
  - Air dried to constant moisture
  - Seived <0.5 mm
  - Packed into 3.5 cm ring cup
Experimental Design

- Biochar Sample Preparation
  - Seived <0.5 mm
  - Packed into 3.5 cm ring cup
Experimental Design

- Sample Scanning - duplicates
- Absorption (reflectance) spectra obtained with NIRSystems 6500 instrument 400-2500 nm
Experimental Design

⊗ Spectral Treatments
  ⊗ scatter corrected to reduce particle size effects
  ⊗ first derivatized to remove noise and bias
  ⊗ pure and difference biochar spectra dissimilar
Experimental Design

Data Treatments

- Converted to % carbon from g kg\(^{-1}\), kg ha\(^{-1}\)

- Normalized to reduce autocorrelation between total C and biochar C

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Column N=144</th>
<th>Field N=216</th>
<th>% BiocharC</th>
<th>% BiocharC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control TRT0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TRT1</td>
<td>5</td>
<td>6987.84</td>
<td>0.36</td>
<td>0.31</td>
</tr>
<tr>
<td>TRT2</td>
<td>10</td>
<td>13184.6</td>
<td>0.72</td>
<td>0.59</td>
</tr>
<tr>
<td>TRT3</td>
<td>20</td>
<td>-</td>
<td>1.43</td>
<td>-</td>
</tr>
</tbody>
</table>

TotalC\(_{\text{norm}}\) = TotalC – BiocharC

BiocharC\(_{\text{norm}}\) = BiocharC / (TotalC – BiocharC)

- Control samples isolated to model total C (TotalC\(_{\text{ctrl}}\))
Experimental Design

伊始，要测试 $H_0a$（近红外光谱（NIRS）不能定量生物炭）

- NIRS PLS 预测模型和统计
- ANOVA 用于预测 C:N 比例在处理之间的差异

接着，要测试 $H_0b$（NIRS 不能区分生物炭 C）

- PCA 组分相关性（非正式支持性）
- 测试模型的 $R^2$ 与生物炭 C 自相关性 ($R^2$) 与总 C
Results

- Data Treatments Column Samples
  - Converted to % C (m/m)
  - Normalized to reduce autocorrelation between biochar C and total C

Insert image of graphs showing correlation between total carbon and biochar carbon with different normalizations and corresponding R² values.
Results

- Data Treatments Field Samples
  - Converted to % C (m/m)
  - Normalized to reduce autocorrelation between biochar C and total C
Results

Distributions – unequal variances between sets

Distribution of % TotalCctrl, % TotalC, % TotalCnorm

Column Samples

Distribution of % BiocharC, % BiocharCnorm

Column Samples

Distribution of % TotalCctrl, % TotalC, % TotalCnorm

Field Samples

Distribution of % BiocharC, % BiocharCnorm

Field Samples
Results

- PLS Model – Column Samps
- SECV = standard error of cross-validation
- RPD = STDEV / SECV

<table>
<thead>
<tr>
<th>Constituent</th>
<th>N</th>
<th>RSQ</th>
<th>SECV</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TotalCctrl</td>
<td>34</td>
<td>0.69</td>
<td>0.05</td>
<td>1.56</td>
</tr>
<tr>
<td>TotalC</td>
<td>138</td>
<td>0.97</td>
<td>0.10</td>
<td>5.56</td>
</tr>
<tr>
<td>TotalCnorm</td>
<td>139</td>
<td>0.51</td>
<td>0.09</td>
<td>1.31</td>
</tr>
<tr>
<td>BiocharC</td>
<td>141</td>
<td>0.99</td>
<td>0.05</td>
<td>9.77</td>
</tr>
<tr>
<td>BiocharCnorm</td>
<td>136</td>
<td>0.99</td>
<td>0.04</td>
<td>7.25</td>
</tr>
<tr>
<td>CN</td>
<td>142</td>
<td>0.94</td>
<td>0.68</td>
<td>3.91</td>
</tr>
</tbody>
</table>

![Graph of NIRS Predicted % BiocharCnorm vs Measured % BiocharCnorm](image1)

![Graph of NIRS Predicted % TotalC vs Measured % TotalC](image2)
## Results

### PLS Model – Field Samples

<table>
<thead>
<tr>
<th>Field Samples</th>
<th>N</th>
<th>RSQ</th>
<th>SECV</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TotalC</td>
<td>212</td>
<td>0.84</td>
<td>0.23</td>
<td>2.40</td>
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<tr>
<td>TotalCnorm</td>
<td>211</td>
<td>0.82</td>
<td>0.24</td>
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<tr>
<td>BiocharC</td>
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<td>2.42</td>
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<tr>
<td>BiocharCnorm</td>
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<td>0.84</td>
<td>0.05</td>
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<tr>
<td>CN</td>
<td>207</td>
<td>0.73</td>
<td>0.78</td>
<td>1.86</td>
</tr>
</tbody>
</table>

![Graph showing NIRS Predicted % BiocharCnorm vs Measured % BiocharCnorm (m/m)](image1)

![Graph showing NIRS Predicted % TotalC vs Measured % TotalC (m/m)](image2)

R² = 0.8436

R² = 0.8500
## Results

- **Validation Field Model**
  - 6 spectral outliers (GH>48)
  - SEPC & RPD = Bias corrected

### Column Samples vs Field Models

<table>
<thead>
<tr>
<th>Constituent</th>
<th>N</th>
<th>Ave GH</th>
<th>SEP</th>
<th>SEPC</th>
<th>RSQ</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TotalCctrl</td>
<td>34</td>
<td>9.08</td>
<td>0.63</td>
<td>0.1</td>
<td>0.3</td>
<td>0.87</td>
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<tr>
<td>TotalC</td>
<td>138</td>
<td>6.88</td>
<td>0.43</td>
<td>0.27</td>
<td>0.88</td>
<td>2.08</td>
</tr>
<tr>
<td>TotalCnorm</td>
<td>138</td>
<td>6.88</td>
<td>0.59</td>
<td>0.16</td>
<td>0.03</td>
<td>0.81</td>
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<tr>
<td>BiocharC</td>
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<td>6.88</td>
<td>0.34</td>
<td>0.22</td>
<td>0.93</td>
<td>2.46</td>
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<td>BiocharCnorm</td>
<td>138</td>
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<td>0.29</td>
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<tr>
<td>CN</td>
<td>138</td>
<td>6.88</td>
<td>4.03</td>
<td>1.36</td>
<td>0.77</td>
<td>2.01</td>
</tr>
</tbody>
</table>

### Validation BiocharCnorm Column Samples vs Field Model

- $R^2 = 0.8740$

### Validation TotalC Column Samples vs Field Model

- $R^2 = 0.8768$
Results

❖ Validation Column Model

❖ SEPC/RPD = Bias corrected

<table>
<thead>
<tr>
<th>Constituent</th>
<th>N</th>
<th>Ave GH</th>
<th>SEP</th>
<th>SEPC</th>
<th>RSQ</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TotalCctrl</td>
<td>72</td>
<td>17.86</td>
<td>0.57</td>
<td>0.50</td>
<td>0.39</td>
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<tr>
<td>TotalC</td>
<td>216</td>
<td>17.67</td>
<td>0.44</td>
<td>0.44</td>
<td>0.43</td>
<td>1.32</td>
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<tr>
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<td>0.75</td>
<td>0.63</td>
<td>0.02</td>
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<tr>
<td>BiocharC</td>
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<td>17.67</td>
<td>0.45</td>
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<td>0.55</td>
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<td>BiocharCnorm</td>
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<td>0.23</td>
<td>0.14</td>
<td>0.35</td>
<td>0.88</td>
</tr>
<tr>
<td>CN</td>
<td>216</td>
<td>17.67</td>
<td>3.83</td>
<td>3.36</td>
<td>0.31</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Results

🌞 Model Predictions vs Sample Moisture:

🌞 Very little or no correlation

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Column Samples</th>
<th>Field Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Cal Prediction</td>
</tr>
<tr>
<td>TotalCctrl</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
<td>TotalC</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>TotalCnorm</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>BiocharC</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>BiocharCnorm</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>CN</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Results

- **C:N Analysis of Variance**

- Significant differences (95% confidence) except 1 validation comparison

<table>
<thead>
<tr>
<th>Predicted C:N</th>
<th>TRT0vTRT1</th>
<th>TRT1vTRT2</th>
<th>TRT2vTRT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Col vs Col_model</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Col vs Fld_model</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fld vs Fld_model</td>
<td>0.000</td>
<td>0.000</td>
<td>-</td>
</tr>
<tr>
<td>Fld vs Col_model</td>
<td>0.006</td>
<td>0.145</td>
<td>-</td>
</tr>
</tbody>
</table>

Column Samples with Field Model

Predicted C:N
Results

PCA-Constituent Correlations

- TotalC/BiocharC/BiocharCnorm similar in column samples only
- TotalCctrl/TotalCnorm similar

<table>
<thead>
<tr>
<th>Highest Correlated PCs</th>
<th>Column Samples 8 PCs</th>
<th>Field Samples 9 PCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>TotalCctrl</td>
<td>3,5,4</td>
<td>1,7,3</td>
</tr>
<tr>
<td>TotalC</td>
<td>1,2,4</td>
<td>1,5,7</td>
</tr>
<tr>
<td>TotalCnorm</td>
<td>5,3,6</td>
<td>1,7,3</td>
</tr>
<tr>
<td>BiocharC</td>
<td>1,2,4</td>
<td>5,3,2</td>
</tr>
<tr>
<td>BiocharCnorm</td>
<td>1,2,4</td>
<td>5,3,2</td>
</tr>
<tr>
<td>C:N</td>
<td>1,2,4</td>
<td>5,1,3</td>
</tr>
<tr>
<td>Moisture</td>
<td>2,4,8</td>
<td>2,9,4</td>
</tr>
</tbody>
</table>
Results

- $R^2$ test – testing H0b

(Autocorrelation between BiocharCnorm and TotalC)

VS

(Correlation between BiocharCnorm reference and NIRS predicted value)
Results

- $R^2$ test – testing $H_0b$

- $R^2 = 0.89$

- $R^2 = 0.8863$

- $z = 13.37$
- $P = 0.000$

- $R^2 = 0.99$

- $R^2 = 0.92$

- $z = 2.10$
- $P = 0.036$
Conclusions

- Biochar can be quantified by NIRS (reject H0a) as shown by:
  - Column & Field PLS model Cross-validation statistics (RPD>2)
  - Field PLS model validation (RPD©>2)

- NIRS can distinguish biochar C and total C (reject H0b) as shown by:
  - Predicted $R^2$ significantly greater than autocorrelation
Acknowledgements

THANK YOU!

- Dr. David Laird
- Dr. Charles Hurburgh, Jr.
- Dr. Kenneth Moore
- MS Agronomy Faculty and Staff
- Dr. David Sevenich
- Family Support Network