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# Quantitative Prediction of Biochar Soil Amendment by Near-Infrared Reflectance Spectroscopy


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**Justification for Research:**
Any sale of C credits in a cap and trade market system or government green payments based on soil biochar applications will require an effective and inexpensive audit system.

**Objective:**
Determine whether Near Infrared Diffuse Reflectance Spectroscopy (NIRS) can distinguish between biochar carbon and biogenic soil organic carbon.

**Methods:**
*Soil samples:* Two independent sets of soil samples were collected from an agricultural field in Boone County, Iowa. The "*column set*" was used previously in a soil column study. The column samples had low diversity of soil properties but contained precisely measured amounts of biochar. The "*field set*" were samples from a field plot study that had been amended with biochar in 2007. The field samples had high intrinsic diversity of soil properties but concentrations of biochar in the field samples was known with less precision.

*NIRS analysis:* Aid-dry samples were analyzed using a Perstorp NIR System 6500 Spectrophotometer between 400 and 2500 nm at 2 nm intervals. The spectra were first truncated (1100-2500 nm), scatter corrected, and then transformed into first derivative spectra and reduced to an 8 nm interval (processed spectra).

*Statistical analysis:* Principal component analysis (PCA) was used to assess the potential of NIRS to discriminate levels of biochar amendments. Partial Least Squares Regression (PLSR) was employed to relate the processed NIRS absorption spectra with the soil carbon concentrations and to derive models for predicting carbon concentrations of unknown samples. To reduce the effects of autocorrelation, the chemical data were normalized before statistical analysis.

TotalCnorm = TotalC – BiocharC

BiocharCnorm = BiocharC / (TotalC - BiocharC)

Where "BiocharC" as the amount of biochar C added to a sample and "TotalC" as the measured amount of total C in the sample expressed as a mass percentage basis. "TotalCnorm" is effectively the concentration of biogenic soil organic C in the sample, and "BiocharCnorm" is effectively the ratio of biochar C to biogenic soil organic C.

**Results:**

Table 1: Basic statistics for C concentrations in the field and column samples.

| | % TotalCctrl Column N=36 | % TotalCctrl Field N=72 | % TotalC Column N=144 | % TotalC Field N=216 | % TotalCnorm Column N=144 | % TotalCnorm Field N=216 |
|---|---|---|---|---|---|---|
| Mean | 2.02 | 2.40 | 2.65 | 2.61 | 2.02 | 2.31 |
| Stdev | 0.10 | 0.57 | 0.54 | 0.59 | 0.13 | 0.56 |
| CV | 5.02 | 23.88 | 20.47 | 22.47 | 6.23 | 24.42 |

Figure 1: Relationships between total C and Biochar C concentrations in the field and column samples. Normalization greatly reduced autocorrelation for the column samples but had little effect on the field samples due to the high intrinsic variability of the field samples.

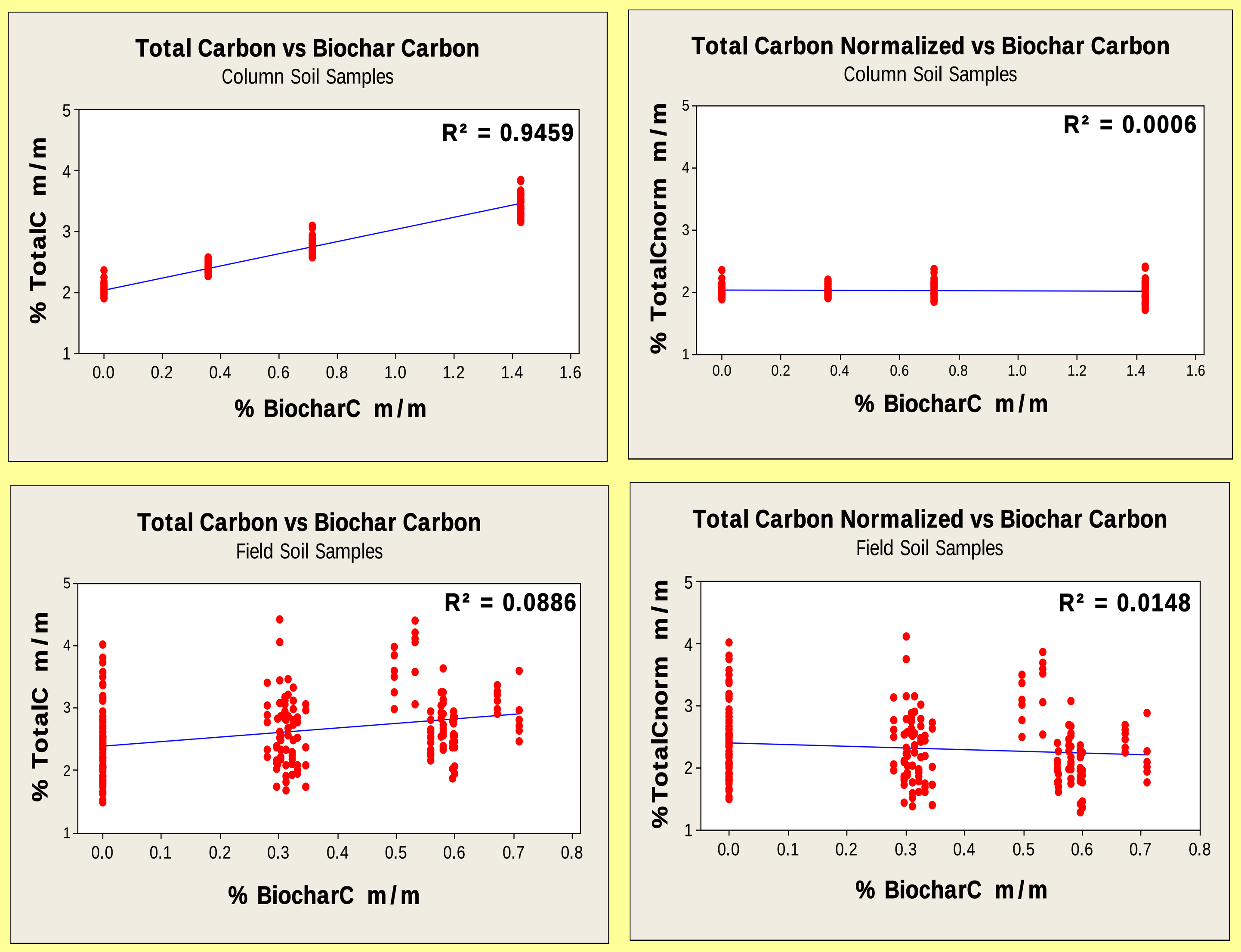


Figure 2: Principal component analysis demonstrates the ability of NIRS to discriminate levels of biochar added to the column and field sample sets.

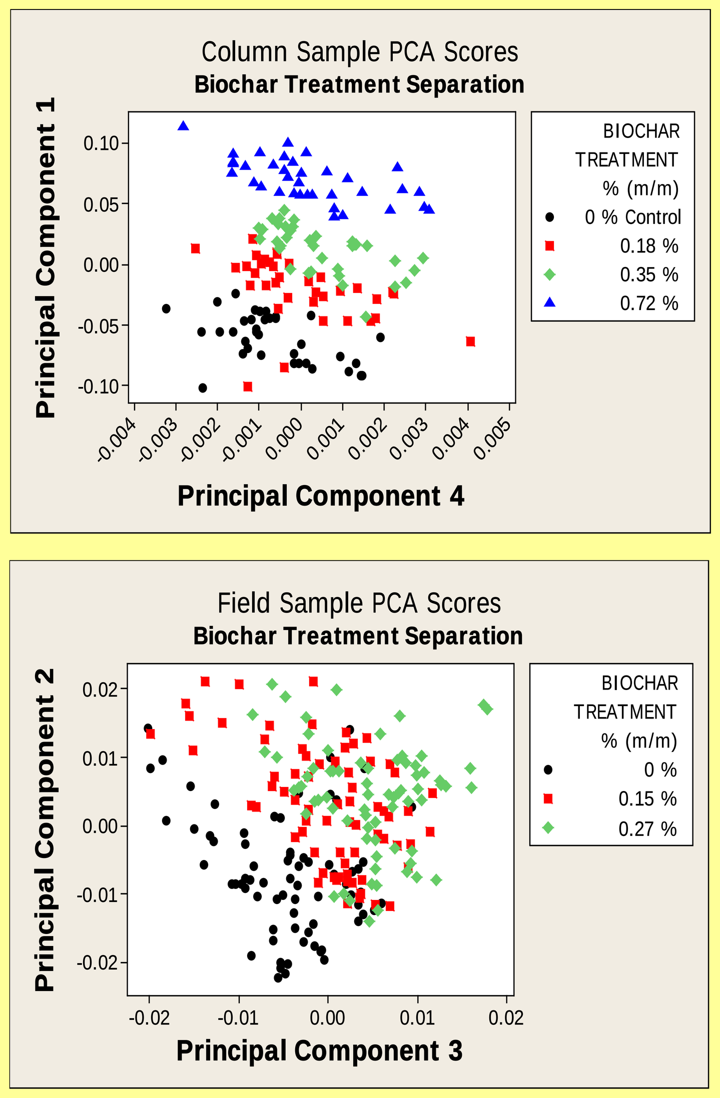


Figure 3: Relationships between measured and PLSR predicted total C, biochar C, and C:N ratios for the field samples. C:N ratios are strongly influenced by biochar amendments hence PLSR prediction of C:N ratios is an independent assessment of the ability of NIRS to discriminate Biochar C.

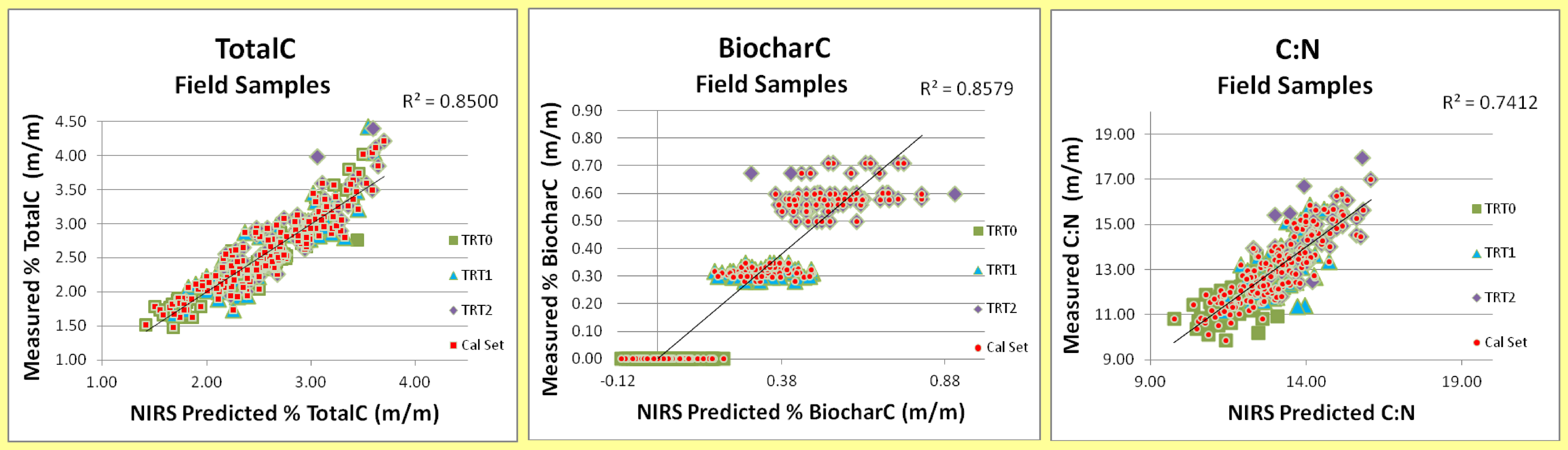


Table 2: Statistics for calibration of the PLSR model using the field sample set.

| Field Samples | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Constituent | N | Components | Mean | SD | Est. Min | Est. Max | SEC | RSQ | SECV | RPD |
| TotalCctrl | 68 | 7 | 2.32 | 0.48 | 0.88 | 3.77 | 0.13 | 0.93 | 0.16 | 2.96 |
| TotalC | 212 | 8 | 2.58 | 0.56 | 0.92 | 4.25 | 0.22 | 0.84 | 0.23 | 2.40 |
| TotalCnorm | 211 | 8 | 2.28 | 0.52 | 0.71 | 3.86 | 0.22 | 0.82 | 0.24 | 2.22 |
| BiocharC | 213 | 7 | 0.30 | 0.24 | 0.00 | 1.02 | 0.09 | 0.85 | 0.10 | 2.42 |
| BiocharCnorm | 205 | 6 | 0.13 | 0.12 | 0.00 | 0.48 | 0.05 | 0.84 | 0.05 | 2.35 |
| CN | 207 | 6 | 12.99 | 1.44 | 8.66 | 17.33 | 0.75 | 0.73 | 0.78 | 1.86 |

Figure 4: Relationship between measured and predicted values of biochar C, biochar C normalized and C:N ratios for the column samples obtained using the PLSR model developed with the field sample set. The results provide an independent validation of the model.

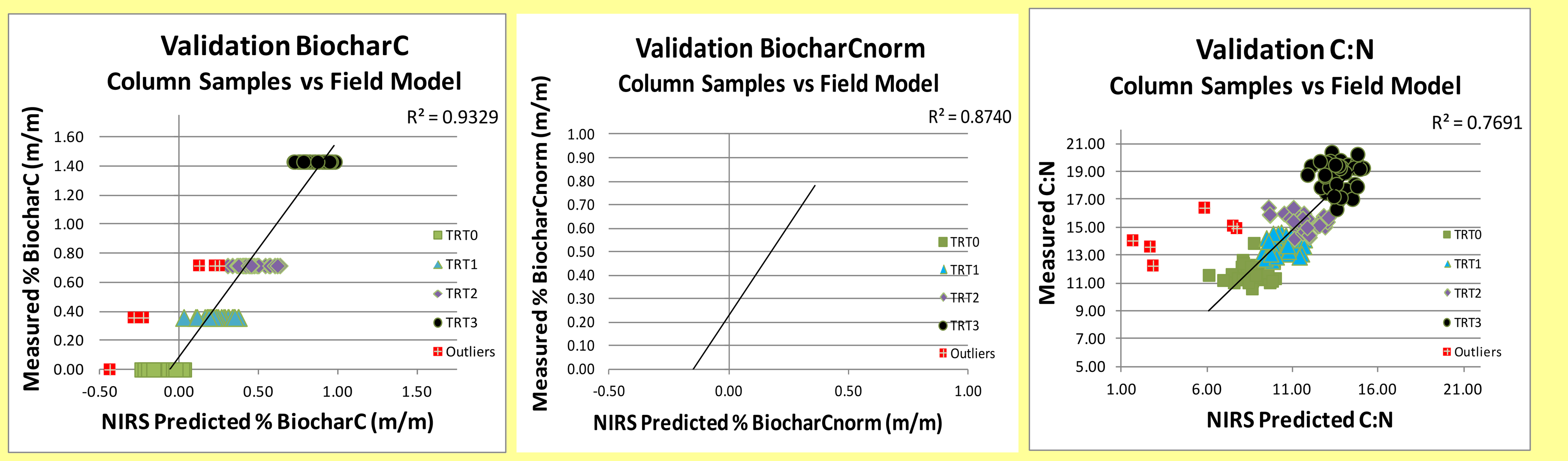


Table 3: Statistics for validation of the PLSR model developed using the field sample set.

| Column Samples vs Field Models | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Constituent | N | Ave GH | Mean | Stdev | SEP | SEPC | RSQ | RPD |
| TotalCctrl | 34 | 9.08 | 2.01 | 0.08 | 0.63 | 0.10 | 0.30 | 0.87 |
| TotalC | 138 | 6.88 | 2.66 | 0.55 | 0.43 | 0.27 | 0.88 | 2.08 |
| TotalCnorm | 138 | 6.88 | 2.03 | 0.13 | 0.59 | 0.16 | 0.03 | 0.81 |
| BiocharC | 138 | 6.88 | 0.63 | 0.54 | 0.34 | 0.22 | 0.93 | 2.46 |
| BiocharCnorm | 138 | 6.88 | 0.31 | 0.27 | 0.29 | 0.13 | 0.87 | 2.06 |
| C:N | 138 | 6.88 | 14.89 | 2.72 | 4.03 | 1.36 | 0.77 | 2.01 |

**Conclusions:**
The calibration indicated the ability of NIRS to model % total C and % biochar C along with their normalized values quantitatively with $R^2$s > 0.82 and RPDs > 2.2, except when modeling total C of the isolated no-biochar controls ($R^2$ = 0.69, RPD = 1.56) and normalized total C ($R^2$ = 0.51, RPD = 1.31) from the low diversity sample set. Validation using the independent PLSR models of the high diversity sample set to predict carbon concentrations for the low diversity sample set showed predictions of % total C, % biochar C, and normalized % biochar C with bias corrected RPDs > 2.1 and $R^2$s > 0.87. Not surprisingly, poor predictions ($R^2$ < 0.55, RPD < 1.32) were obtained using the PLSR models for the low diversity sample set to predict carbon concentrations for the high diversity sample set (data not shown). Analysis of variance for predicted C:N ratios showed significant differences (alpha < 0.05) between biochar treatments and, independently, NIR's ability to respond to biochar treatments. The model validation $R^2$ (0.92) between the measured normalized biochar C and model-predicted biochar C was significantly greater (alpha<0.05) than the autocorrelation between the measured total C and biochar C ($R^2$ = 0.89), thus demonstrating that NIRS responds to biochar C apart from total C. The results indicate that inexpensive NIRS analyses can be used to audit soil biochar applications.