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Simulated *in situ* soil carbon measurements using laser-induced breakdown spectroscopy (LIBS).

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Abstract

Laser-induced Breakdown Spectroscopy (LIBS) is an emerging technology that has the potential to provide rapid, accurate and precise elemental analysis of soil constituents, such as carbon, *in situ* across landscapes. In this study, we evaluated the accuracy of simulated *in situ* LIBS proximal sensing for measuring soil profile carbon. We interrogated 78 intact soil cores (3.8 cm x 50 cm) from three north central Montana, USA wheat fields with four soil samples from each core analyzed for soil total carbon (TC), inorganic carbon (IC), and soil organic carbon (SOC). Partial least squares (PLSR) calibration models were built using 58 cores (227 samples) and independently validated with the remaining 20 cores (79 samples). We obtained the best LIBS predictions for total carbon (r^2 = 0.68, SEP = 5.8 g kg^{-1}, RPD = 1.6 g kg^{-1}) followed by inorganic carbon (IC) (r^2 = 0.60, SEP = 5.8 g kg^{-1}, RPD = 1.5 g kg^{-1}) and SOC (r^2 =0.19, RPD=1.0 g kg^{-1}, SEP = 3.4 g kg^{-1}). Soil organic carbon r^2, RPD, as expected, were lower than those for total and inorganic C; however SEP was also lower. These findings were due, in part, to 1) the narrow LIBS spectral range that did not capture elements related to SOC (i.e. O, H, and N), and 2) low SOC variability (σ = 3.47 g kg^{-1}), with laboratory reference measurement error (SEL = 1.37 g kg^{-1}) estimated at ~ 40% of σ_{SOC}. Partial least squares regression coefficients suggested stoichiometric relationships between C (247.8 nm) and other elements related to total and inorganic carbon [Mg (279.55-280.4 nm, 285.26 nm) and Si (251.6 nm, 288.1 nm)]. These results show great promise for deploying LIBS for *in situ* soil carbon determination. To our knowledge, this is the first rigorous independent validation of LIBS predictions reported for a significant number of intact soil cores.

Keywords: proximal soil sensing, laser-induced breakdown spectroscopy, soil matrix effects, partial least squares regression, soil carbon

1. Introduction

There is growing need for rapid, accurate, and inexpensive methods to measure and verify soil organic carbon (SOC) sequestration for national greenhouse gas accounting and the development of a soil carbon trading market (Council, 1999; Gehl and Rice, 2007). In particular, techniques for the rapid measurement of SOC *in situ* are required (Christy, 2008; Gehl and Rice, 2007). Laser-induced breakdown spectroscopy (LIBS) is an emerging spectroscopic technique for rapid quantification of soil carbon and other soil constituents (Cremers et al., 2001; Ebinger et al., 2003; Martin et al., 2007; Martin et al., 2003; Martin et al., 2004). Moreover, the LIBS instrument is capable of being mounted in a soil penetrometer (Mosier-Boss et al., 2002) which could be deployed for rapid soil profile characterization and mapping at field and landscape scales.

Laser-induced breakdown spectroscopy (LIBS) is based on atomic emission spectroscopy and involves directing a focused Nd:YAG laser onto the surface of a target material (Radziemski and Cremers, 1989). The focused laser ablates a small amount of surface material producing expanding plasma containing electronically excited ions, atoms, and small molecules. As these excited species relax to lower electronic states they emit light at wavelengths indicative of the elemental composition of the ablated sample. Some of the emission is captured by a fiber optic cable and directed into a dispersive spectrometer and charge coupled detector (CCD) (Clegg et al., in press; Cremers et al., 2001; Ebinger et al., 2003; Martin et al., 2003; Radziemski and Cremers, 1989; Thompson et al., 2006). The resulting data are spectrally rich with distinct emission lines for most atoms and ions present in the ablated material.

Univariate calibration of LIBS spectra are generally complicated by the chemical matrix effects. Chemical matrix effects have been defined as chemical properties of the interrogated sample that impact the relationship between emission line intensity or area and the element in the

60 sample responsible for producing that line (Cremers and Radziemski, 2006; Eppler et al., 1996;
61 Gornushkin et al., 2002; Häkkänen and Korppi-Tommola, 1998). More specifically, matrix
62 effects are related to elemental and molecular composition of the sample, plasma composition,
63 within plasma interactions, and laser-sample coupling efficiency. Previously published studies
64 have attempted to compensate for these matrix effects and increase predictive accuracy using
65 several approaches. For example, peak height or peak area of standards with known composition
66 have been used to calibrate models; normalization of LIBS spectra to total emission intensity;
67 normalization of peak height or area to another spectral feature; employing a plasma physics
68 model without the use of calibration curves (i.e. calibration-free LIBS); using multiple
69 interrogations per sample, and spectral averaging for calibration and and/or validation (Clegg et
70 al., in press; Cremers and Radziemski, 2006; Ebinger et al., 2003; Martin et al., 2007; Martin et
71 al., 2003; Salle et al., 2006; Thompson et al., 2006; Yaroshchyk et al., 2006).
72 With proper calibration, LIBS produces a precise and selective method for measuring
73 metal ions such as Pb, Be, Cr, and Sr in paint and soils (Sirven et al., 2006; Yamamoto et al.,
74 1996), nitrogen, Pb, and Ba in sand (Eppler et al., 1996; Harris et al., 2004), and Cu, Zn, and As
75 in wood preservatives (Martin et al., 2005). Though there have been relatively few applications
76 of LIBS for soil carbon determination, published calibrations show LIBS spectra to be well
77 correlated with standard dry combustion measurements of soil carbon with reported r^2 values of
78 0.56 to 0.99 (Cremers et al., 2001; Ebinger et al., 2003; Martin et al., 2007; Martin et al., 2003).
79 This study is the first known attempt to differentiate inorganic soil C from SOC for soil samples
80 without pre-treatments
81 There has been little independent validation of published LIBS calibrations on a large
82 number of soil samples. Cremers et al. (2001) used a subset of 12 Colorado agricultural soil
83 samples from conventionally tilled farms to calibrate a LIBS model ($r^2 = 0.96$) and verified the

84 model with a different subset (N=8) of the same Colorado soils as well as soils from Los
85 Alamos, NM (N=10) that formed in different parent materials. Ebinger et al.(2003) used 6
86 randomly chosen soil samples from a dataset of 18 samples collected from three Colorado farm
87 fields to calibrate a model ($r^2 = 0.99$) then used the model to predict the remaining 12 samples (r^2
88 = 0.95). It is not yet standard practice in LIBS spectroscopy to 'hold-out' independent samples
89 for validation (Martin et al., 2007; Martin et al., 2003; Martin et al., 2004). While published
90 research shows the potential of LIBS for SOC determination, further work is required with larger
91 sample sets and more rigorous model validation.
92 The soil samples employed in these published studies were also pre-treated prior to LIBS
93 interrogation. Pre-treatments included: air-drying, sieving and packing in quartz tubes (Cremers
94 et al., 2001); pelletizing under pressure (Martin et al., 2007; Martin et al., 2004); and treating
95 with acid to remove carbonates, pelletizing in a tube, and air-drying (Martin et al., 2003).
96 Though LIBS has been proposed as an *in situ* SOC measurement tool (Gehl and Rice, 2007), it
97 remains to be demonstrated that *in situ* results will match those obtained with prepared samples.
98 In this study we evaluated the accuracy of simulated *in situ* LIBS proximal sensing for
99 soil profile carbon measurement. We employed various methods and tools for LIBS evaluation
100 including 1) model calibration with large numbers of samples, 2) partial least squares regression
101 (PLSR) modeling of spectrally averaged LIBS interrogation points, 3) independent validation of
102 soil total, inorganic and organic carbon PLSR models, and 4) examination of PLSR regression
103 coefficients.

104 **2. Material and Methods**

105 **2.1 Study Area**

106 We chose the "Golden Triangle" region of north central Montana, USA as our research
107 study area. This region is characterized by soils formed in glacial till on gently rolling

topography. Soils were not highly weathered and were typically calcareous within 0.5 m of the surface. Aridic intergrades of frigid, ustic, Mollisols, Entisols, and Inceptisols predominated. Cropping systems in the study area were generally reduced tillage small grain-fallow rotations with a significant acreage managed by direct-seeding or no-till. All three sampling sites had a general cropping history of cultivation beginning in the 1920's progressing to wheat-fallow rotations with multiple tillage operations per year and finally conversion to a direct-seeded wheat-fallow rotation between 2004 and 2005.

2.2 Soil Sampling

The selection of soil coring locations was based upon surface soil Visible and Near-Infrared (VisNIR) reflectance acquired for a parallel study focused on that technology. In 2006, 78 intact cores were obtained from three 16.2 ha sub-fields in north central Montana with locations show in Figure 1. Intact, 4.45 cm diameter by 50 cm deep soil cores were extracted using a truck-mounted hydraulic soil sampling tube fitted with removable plastic sleeves (Giddings Machine Co., Windsor, CO). The field-moist intact cores were transported back to the laboratory and stored under refrigeration prior to interrogation.

2.3 Core Interrogation and PLSR Analysis

We interrogated intact soil cores to simulate *in situ* soil characterization following the general protocol of Waiser et al. (2007). Each field moist core was interrogated at 8 depths through ~ 3 x 3 cm windows cut in the plastic core sleeve (Fig. 2). A prototype LANL LIBS Core Scanning (LIBS-CS) instrument was used to probe the samples in an argon purged environment at 2.5, 7.5, 12.5, 17.5, 22.5, 27.5, 35, and 45 cm (+/- 1.5 cm) along each intact soil core with 9 interrogation spots per depth. The LIBS-CS instrument employed a Big Sky Laser operating at 10 Hz at approximately 80mJ/pulse. The LIBS spectra were collected with an optical fiber and directed into an Ocean Optics HR2000 spectrometer (200-300 nm, 0.1 nm

132 spectral resolution). These spectrometers are readout noise limited and signal-to-noise ratios
133 improve if emissions from multiple laser shots are used (Clegg et al., in press). For this
134 experiment, we set the spectrometers to a 1 second integration time with 5 averages so that each
135 spectrum represented 50 laser shots. An argon purge was used to reduce the plasma
136 interferences from oxygen and water vapor. A similar argon purge would be operationally
137 feasible for an *in situ* application, a LIBS instrument mounted in a soil penetrometer for
138 example, given the small gas volume needed to purge a 200 μm interrogation point along a soil
139 profile. The LIBS data were normalized prior to spectral model building by dividing each
140 wavelength value by the sum of all wavelength values for each spectrum as detailed by
141 Thompson et al. (2006) and Clegg et al. (in press) and then averaged by depth. Normalization
142 reduces the shot-to-shot variability in LIBS data that has been attributed to soil and chemical
143 matrix effects (Mosier-Boss et al., 2002).
144 Small subsamples of soil (~ 4 g) were taken from all interrogation depths for standard
145 carbon analysis. Using VisNIR spectra for each core, acquired concurrently with LIBS
146 interrogations, samples from the 8 interrogation depths were clustered into 4 spectrally similar
147 groups using Partitioning Around Mediods (Kaufman and Rousseeuw, 1990). One interrogation
148 depth was randomly chosen from each group (78 cores × 4 samples per core = 312 possible) for
149 standard soil carbon analysis using procedures described in Bricklemyer et al. (2005). Total
150 carbon was measured by dry combustion using a LECO TruSpec (LECO Corp., St. Joseph, MI,
151 USA). Inorganic carbon was measured by modified pressure calcimeter method as developed by
152 Sherrod et al. (2002). Soil organic carbon (SOC) was calculated by difference: SOC = TC-IC
153 where TC = total carbon and IC = soil inorganic carbon. Standard carbon measurements were

154 used for LIBS calibration and validation. The final dataset included 306 samples from 78 cores
155 due to incomplete LIBS spectra for samples (Table 1).

156 We randomly selected 58 cores (227 soil samples) to construct LIBS partial least squares
157 regression (PLSR) calibrations for TC, IC and SOC using the R statistical software package
158 "pls" {R, 2008 #19; Wehrens, 2007 #121}. While most previous studies have used carbon peak
159 intensities at either 247.8 nm or 193 nm and univariate statistics to calibrate, recently published
160 results suggest that multivariate statistical approaches such as partial least squares (PLS)
161 regression can yield markedly better calibrations (Clegg et al., in press; Martin et al., 2007). We
162 independently validated these calibrations with the remaining 20 cores (79 samples). With cores
163 from only three fields, we were not able to construct a regional calibration with whole-field
164 cross-validation, so results of this study indicate what is possible with local within-field
165 calibration (Brown et al., 2005).

166 To quantify the effects of fine scale (e.g. mm) soil variability and estimate the minimum
167 number of focused LIBS interrogations required to characterize a 1-2 cm diameter heterogeneous
168 soil material, we randomly selected and averaged 1, 2, 3, 5 and 7 interrogations from the 9
169 acquired at each depth. The previously described processing, modeling and validation
170 procedures were then repeated for each of these "reduced" LIBS interrogation scenarios.

171 The quality of PLSR model fit was evaluated using regression of PLSR predicted vs.
172 reference measurement, squared bias (SB), non-unity of the regression line (NU), and lack of
173 correlation (LC) where mean squared deviation (MSD) = SB+NU+LC (Brown et al., 2005;
174 Gauch et al., 2003). Standard chemometric modeling statistics were calculated for each model,
175 including validation standard error of prediction (SEP) and residual product differential (RPD)
176 (Islam et al., 2003). Standard error of laboratory measurement (SEL) was estimated using

177 replicate TC and IC laboratory measurements as described by Workman (2001) and SOC SEL
178 was calculated using propagation of error estimation following Andraos (1996).
179
180 **3. Results**
181 Summary statistics for TC, IC, and SOC are presented in Table 1. For the samples in this
182 study, TC values did not exceed 57 g kg^{-1}, IC values were less than 46 g kg^{-1}, and SOC values
183 never exceeded 20 g kg^{-1}. Concentrations of IC were most variable in the dataset (σ = 10.18, CV
184 = 107%) follow by TC and SOC (σ = 9.53 and 3.47; CV = 59.6% and 44.4%, respectively). The
185 SEL for reference measurements were estimated at 0.90, 1.03, and 1.37 g kg^{-1} for TC, IC, and
186 SOC, respectively. Reference SOC was least variable where σ_{SOC} was just 2.5 times SEL_{SOC}.
187 Variability in IC was a function of pedogenesis where IC was not present or present in low
188 concentrations in A horizons (top 20 cm) and increased sharply in B horizons, the majority of
189 which occurred below 20 cm. The sharp boundary between the A and B horizons are evident in
190 Figure 2. Variability in SOC was substantially less than IC with highest concentrations of SOC
191 occurring in A horizons and diminished with depth.
192 Full-cross validated calibration model statistics are presented in Table 2. Calibration
193 models for TC and IC achieved quantitative accuracy (RPD=2.1 and 2.3, r^2 = 0.76 and 0.81,
194 respectively); whereas, semi-quantitative results were achieved for SOC (RPD = 1.5, r^2 = 0.55).
195 Calibration SEP values were 5.1 g TC kg^{-1} soil, 4.3 g IC kg^{-1} soil, and 2.5 g SOC kg^{-1} soil.
196 Applying PLSR to LIBS spectra resulted in three distinct calibration models. Regression
197 coefficients from TC, IC, and SOC PLSR calibration models are presented in Figure 3. We
198 found that although TC and IC were strongly related (Fig. 4), the importance of specific
199 elemental emissions in PLSR models were markedly different (Fig. 3). For example, the major
200 C emission at 247.8 nm was an important predictor for TC and SOC (relatively), but was not

201 important for IC. Additionally, several Mg emissions were useful in predicting IC and TC, but,
202 as expected, not for predicting SOC, and Si was important for IC but not TC and SOC. Results
203 suggest that PLSR found meaningful stoichiometric relationships between elements related to
204 various naturally occurring forms of carbon in the soil matrix.

205 For the hold-out validation dataset, the LIBS-CS instrument best predicted total carbon
206 (r^2 = 0.68, RPD = 1.6; Table 3, Fig. 5). Inorganic carbon predictions were nearly as accurate (r^2
207 = 0.60, RPD = 1.5; Table 3, Fig. 5). Predicting SOC appeared unacceptable, as expected (r^2 =
208 0.19, RPD = 1.0; Table 3, Fig. 5); however, r^2 and RPD will both increase with greater
209 variability in the target variable, given a fixed prediction error. Validation SEP values were 5.8
210 g TC kg^{-1} soil, 5.8 g IC kg^{-1} soil, and 3.4 g SOC kg^{-1} soil which were greater than the respective
211 SEL, and lower than standard deviation (σ) of measured TC and IC. Validation SEP and σ were
212 equivalent for SOC and approached SEL_{SOC} (1.37 g kg^{-1}). Partitioning MSD into three
213 components, we found the LIBS TC model had low bias (SB=3.3%) and non-unity (NU=5.6%)
214 (Table 3). The LIBS IC model also had low bias (SB=0.1%); however, non-unity was much
215 greater (NU=19.2%). Bias remained low for the LIBS SOC model (SB=3.7%), but non-unity
216 greatly increased (NU=46.5%; Table 3, Fig. 5). Lack of correlation accounted for the majority
217 of MSD for the LIBS TC and IC models (91.1% and 80.7%, respectively) and nearly half of
218 MSD for the SOC model (49.8%) (Table 3). All RPD values were less than 2.0, which is
219 commonly considered the division between quantitative (RPD≥2) and semi-quantitative (RPD <
220 2) calibrations (Islam et al., 2003).

221 Figure 6 shows the effect of spectrally averaging multiple LIBS interrogation points per
222 sample on TC, IC, and SOC predictions. Spectrally averaging up to 9 interrogation points
223 decreased TC SEP by 18.5% and IC SEP by 8.0%; however SEP was unchanged for SOC.
224 Values for SEP ranged from 5.8 – 7.1 g C kg^{-1} soil for TC, 5.5 – 6.4 g C kg^{-1} soil for IC and 3.4 –

225 3.7 g C kg^{-1} soil for SOC. Similarly, TC and IC RPD values increased by 23.1% and 7%,
226 respectively, whereas RPD was unchanged for SOC. Values for RPD ranged from 1.3 – 1.6 for
227 total C, 1.4 –1.6 for inorganic C, and 0.9 – 1.0 for soil organic C. No appreciable accuracy
228 improvement was observed for spectrally averaging more than 5 LIBS interrogation points per
229 sample (Fig.7).

230 **4. Discussion**

231 The LIBS validation accuracies reported here for TC, IC, and SOC failed to match results
232 from previously referenced studies. We attribute part of the reduction in accuracy to evaluating
233 PLSR models with validation cores (Brown et al., 2005). Calibration model accuracies achieved
234 quantitative (RPD > 2) levels for TC and IC, and semi-quantitative (RPD > 1.5) results for SOC;
235 however testing these models with independent validation samples noticeably degraded
236 predictive accuracy. Semi-quantitative status was barely achieved for TC and IC; whereas SOC
237 was not predicted with useful accuracy. These findings underscore the importance of
238 independent validation for accurate reporting of predictive accuracy for LIBS and other proximal
239 sensing methods.

240 Fine-scale (i.e. sub-cm) variability in carbon content was lower than anticipated. Our
241 results from spectrally averaging 1 – 9 interrogation spots suggest that no more than 5
242 interrogations per sample are required for representative *in situ* measurements of small
243 interrogation volumes (~3 cm^3). This finding also implies that interrogation areas were relatively
244 homogenous with respect carbon content. Each LIBS interrogation was a spectral average of 50
245 laser shots and probed volume of ~ $8x10^{-5}$ cm^3. Averaging 5 interrogation points equated to
246 ~0.02% of the total interrogation volume, a very small proportion; however it is common for a
247 500+ g field soil sample to be representatively subsampled and then 0.02 – 0.2 g (0.004 – 0.04%
248 of total sample) analyzed for C by dry combustion. Five LIBS interrogations may have been

representative of the interrogation volume; however, how representative that volume was of the associated core increment has yet to be determined and will be examined in further analysis of core sections.

It appeared that our PLSR models identified stoichiometric relationships between carbon and elements associated with carbon within the soil matrix. Regression coefficients important to total C included the strong carbon emission line at 247.8 nm, a silicon emission line at 251.6 nm, and several Mg emission lines (no strong Ca emissions found between 200 -300 nm). Total soil carbon, as measured by dry combustion, includes carbon associated with organic compounds as well as inorganic Ca and Mg carbonates ($CaCO_3$ and $MgCO_3$). The Mg emissions were also strong predictors for IC; however, PLSR did not find an important relationship between the 247.8 nm C emission and IC. Instead, a silicon emission at 251.6 nm was strikingly more important for predicting IC compared to TC. The importance of the Si emission was attributed to chemical matrix effects associated with the LIBS method for no stoichiometeric relationship exists between IC and Si.

The relatively narrow spectral range (200-300 nm) of LIBS emissions recorded with the Ocean Optics HR2000 spectrometer also contributed to less precise MVA calibration and validation results. Prior to using PLSR, univariate techniques were used to relate sample carbon content to peak height (or area) of the carbon emission at 247.8 nm, justifying using the 200 – 300 nm spectral range. As discussed above, PLSR found relationships between C and other elements associated with soil C. The narrow spectral range did not capture emissions from several other elements associated with soil inorganic C such as Ca (315.89, 317.93, and 534.95 nm), and organic C such as H (656.27 and 656.29 nm), N (742.3, 744.2, and 746.8nm) and O (777.4nm) that occur at wavelengths greater than 300 nm. Consequently, correlations between C and elements associated with SOC could not be generated with a PLSR model and likely reduced

273 the predictive accuracy for SOC. Clegg et al.(in press) observed that the best calibration models
274 for predicting elemental composition of igneous rocks were generated when the entire LIBS
275 spectrum (200 – 900 nm) was used in PLSR. We anticipate PLSR predictive accuracies for both
276 inorganic and organic carbon will improve when including the entire LIBS spectrum in future
277 soil carbon measurements.

278 Finally, we attribute the remaining accuracy reduction to challenges surrounding *in situ*
279 interrogations of intact cores rather than pressed or prepared samples. Prepared samples have the
280 primary benefit of providing a smooth soil surface for interrogation compared to undisturbed and
281 uneven intact soil core surfaces. Uneven surfaces can cause the distance from the laser focal
282 point to the sample to vary among and within interrogation areas. Naturally occurring fractures
283 and macropores also tend to obstruct the collection optics from observing the plasma emission.
284 Normalization was used to partially compensate for these fluctuations.

285 **4. Conclusions**

286 To the best of our knowledge, this study represents the first rigorous validation of LIBS
287 calibrations using a significant number (78) of intact soil cores without pre-treatment. Using
288 LIBS with a spectral range of 200-300 nm and employing partial least squares regression (PLSR)
289 modeling, we achieved semi-quantitative validation accuracies for total carbon (TC) ($r^2 = 0.68$,
290 RPD = 1.6, SEP = 5.8 g kg^{-1}, SEL = 0.9 g kg^{-1}) and inorganic carbon (IC) ($r^2 = 0.60$, RPD=1.5,
291 SEP = 5.8 g kg^{-1}, SEL = 1.03 g kg^{-1}). Soil organic carbon (SOC) predictions appeared
292 unacceptable (r^2 =0.19, RPD=1.0, SEP = 3.4 g kg^{-1}); however the low validation r^2 and RPD
293 values were primarily due to 1) the incomplete LIBS spectral record covering 200-300 nm, and
294 2) low SOC variability (σ = 3.47 g kg^{-1}) with laboratory reference measurement error (SEL)
295 estimated at 1.37 g kg^{-1} or 40% of σ_{soc}.

296 Regression coefficients from PLSR models suggested that calibrations utilized
297 stoichiometric relationships between C and elements related to C in the soil matrix. Emissions
298 from carbon (247.8 nm), Mg (279.55-280.4 nm, 285.26 nm), and Si (251.6 nm, 288.1 nm) were
299 important predictors for estimating total and inorganic carbon. The relatively narrow spectral
300 range (200 – 300 nm) of the LIBS spectrum recorded in this study; however, omitted emissions
301 from elements related to soil carbon, including Ca, O, H, and N. Increasing the spectral range to
302 the full LIBS spectrum (200 – 900 nm) could increase predictive accuracies for *in situ*
303 measurement of both inorganic and organic C.
304 In addition to expanding the spectral range, we identified three key strategies for
305 improved LIBS *in situ* soil measurements. First, improve the LANL-CS LIBS instrument design
306 to compensate for uneven soil core surfaces. Second, evaluating the ability of LIBS to capture
307 SOC variability will require the acquisition of calibration soil cores with greater SOC variability.
308 Finally, we need to acquire soil cores from a more diverse set of locations to evaluate the
309 potential of developing regional LIBS calibrations. Continued LIBS development and evaluation
310 will assist in realizing the full potential of this emerging spectroscopic technique for *in situ* soil
311 characterization.
312
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318
319

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Table 1. Soil total, inorganic, and organic carbon summary statistics for 78 intact soil cores from three wheat fields in north central MT, 2007.

	Soil Total C	Soil Inorganic C	Soil Organic C
	---------- g kg $^{-1}$ ----------		
Median	15.74	7.95	7.82
Min	1.43	0.00	0.85
Max	56.56	45.27	19.32
Mean	17.09	8.88	8.21
σ	10.18	9.53	3.47
CV	59.6%	107.4%	44.4%
n	306	306	306

σ = standard deviation; CV = coefficient of variation

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Table 2. Laser-induced breakdown spectroscopy (LIBS) partial least squares regression (PLSR) calibration statistics for soil total carbon (TC), inorganic carbon (IC), and organic carbon (SOC).

Model	n	r^2	RPD (g/kg soil)	SEP (g/kg soil)	SB† (%)	NU† (%)	LC† (%)
LIBS TC	79	0.76	2.1	5.1	0.0	24.6	75.4
LIBS IC	79	0.81	2.3	4.3	0.5	28.2	71.3
LIBS SOC	79	0.55	1.5	2.5	0.0	45.0	55.0

RPD = residual product differential, SEP = standard error of prediction, SB = squared bias, NU = non-unity, LC = lack of correlation

† percent of mean squared deviation (MSD)

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Table 3. Laser-induced breakdown spectroscopy (LIBS) partial least squares regression (PLSR) validation statistics for soil total carbon (TC), inorganic carbon (IC), and organic carbon (SOC).

Model	n	r^2	RPD (g/kg soil)	SEP (g/kg soil)	SB† (%)	NU† (%)	LC† (%)
LIBS TC	79	0.68	1.6	5.8	3.3	5.6	91.1
LIBS IC	79	0.60	1.5	5.8	0.1	19.2	80.7
LIBS SOC	79	0.19	1.0	3.4	3.7	46.5	49.8

RPD = residual product differential, SEP = standard error of prediction, SB = squared bias, NU = non-unity, LC = lack of correlation

† percent of mean squared deviation (MSD)

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420

421 **Figure Captions**

422

423 **Figure 1.** Geographical location of the study area with three selected farm fields (a), and
424 randomly selected calibration (triangles) and validation (circles) core locations at the LYD (b),
425 HOR (c), and MAT (c) sites.

426

427 **Figure 2.** LIBS sampling depths on a representative intact soil core and LIBS interrogation point
428 configuration within a depth sample (inset).

429

430 **Figure 3.** Partial least squares regression (PLSR) coefficients for soil total, inorganic, and
431 organic carbon. The magnitude of the coefficients indicates the relative importance of each
432 emission line. Dashed vertical lines indicate important elemental emission lines for predicting
433 the various forms of soil carbon.

434

435 **Figure 4.** Regression of soil total carbon for predicting soil inorganic carbon. Soil IC represents
436 a large portion of total C in these semi-arid glacial till soils.

437

438 **Figure 5.** Independent validation of predicted soil total carbon (TC), inorganic carbon (IC), and
439 organic carbon (SOC) using LIBS and partial least squares regression models. Nine
440 interrogation spectra were averaged for PLSR analysis.

441

442 **Figure 6.** The effect of spectrally averaging multiple LIBS interrogation points on the predictive
443 accuracy of soil total carbon (TC), inorganic carbon (IC), and organic carbon (SOC).

444

Figure 1.

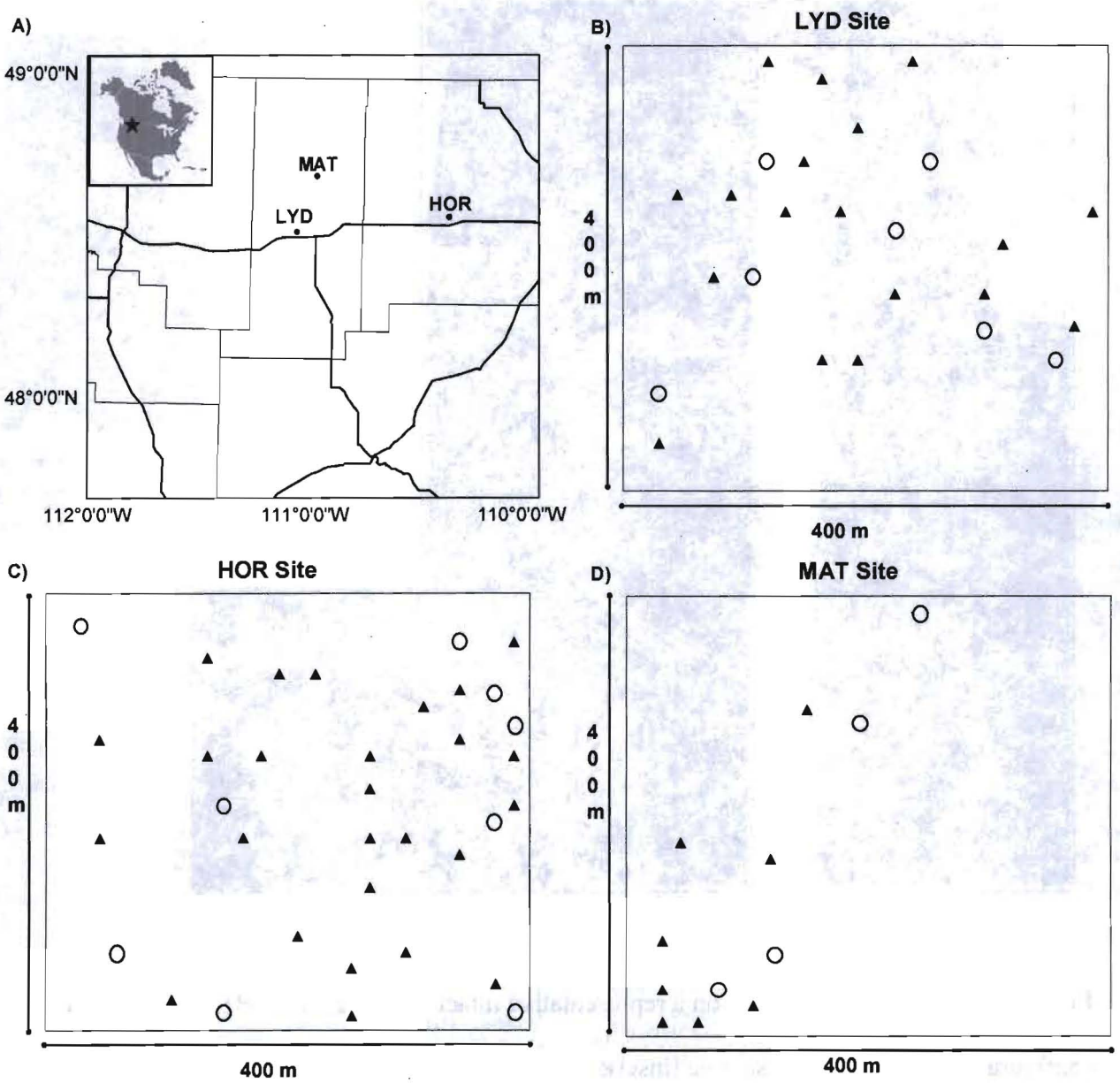


Figure 1. Geographical location of the study area with three selected farm fields (A), and randomly selected calibration (triangles) and validation (circles) core locations at the LYD (B), HOR (C), and MAT (D) sites.

Figure 2

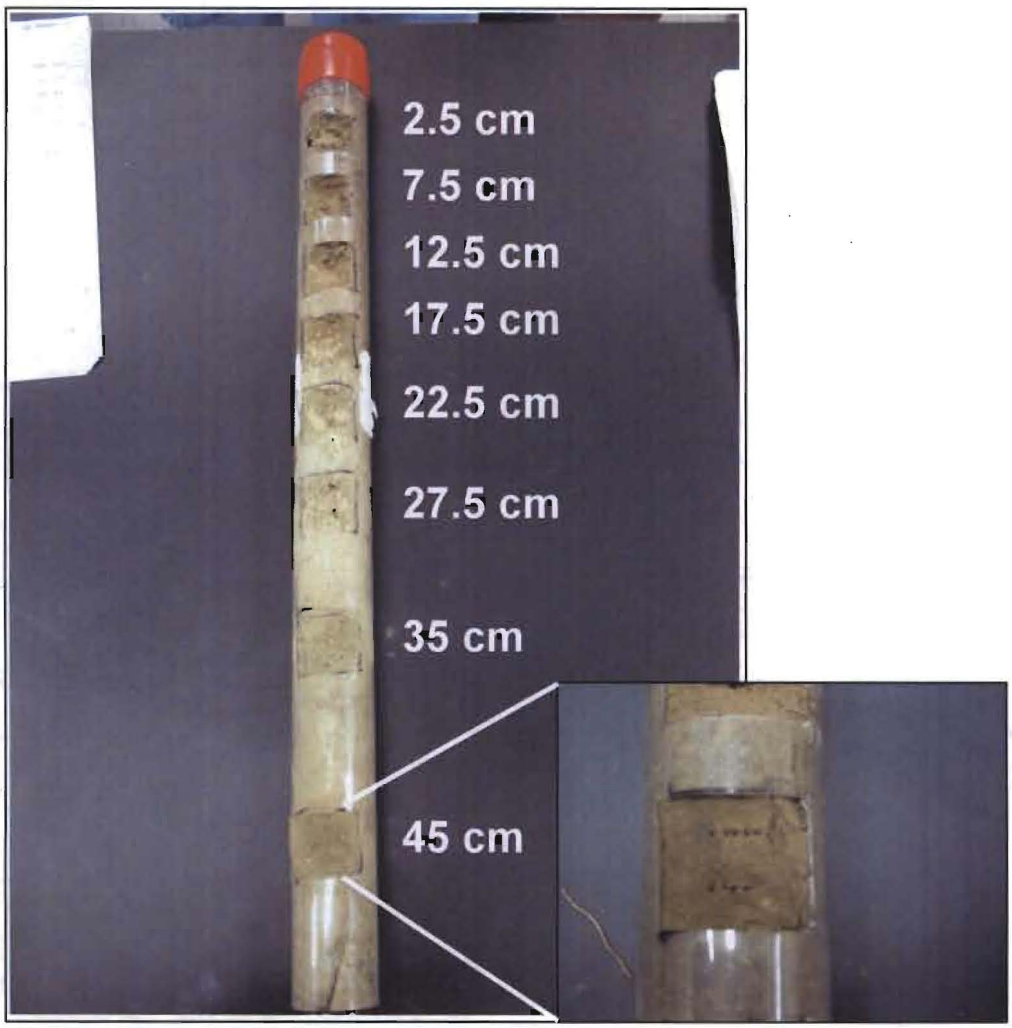


Figure 2. LIBS sampling depths on a representative intact soil core and LIBS interrogation point configuration within a depth sample (inset).

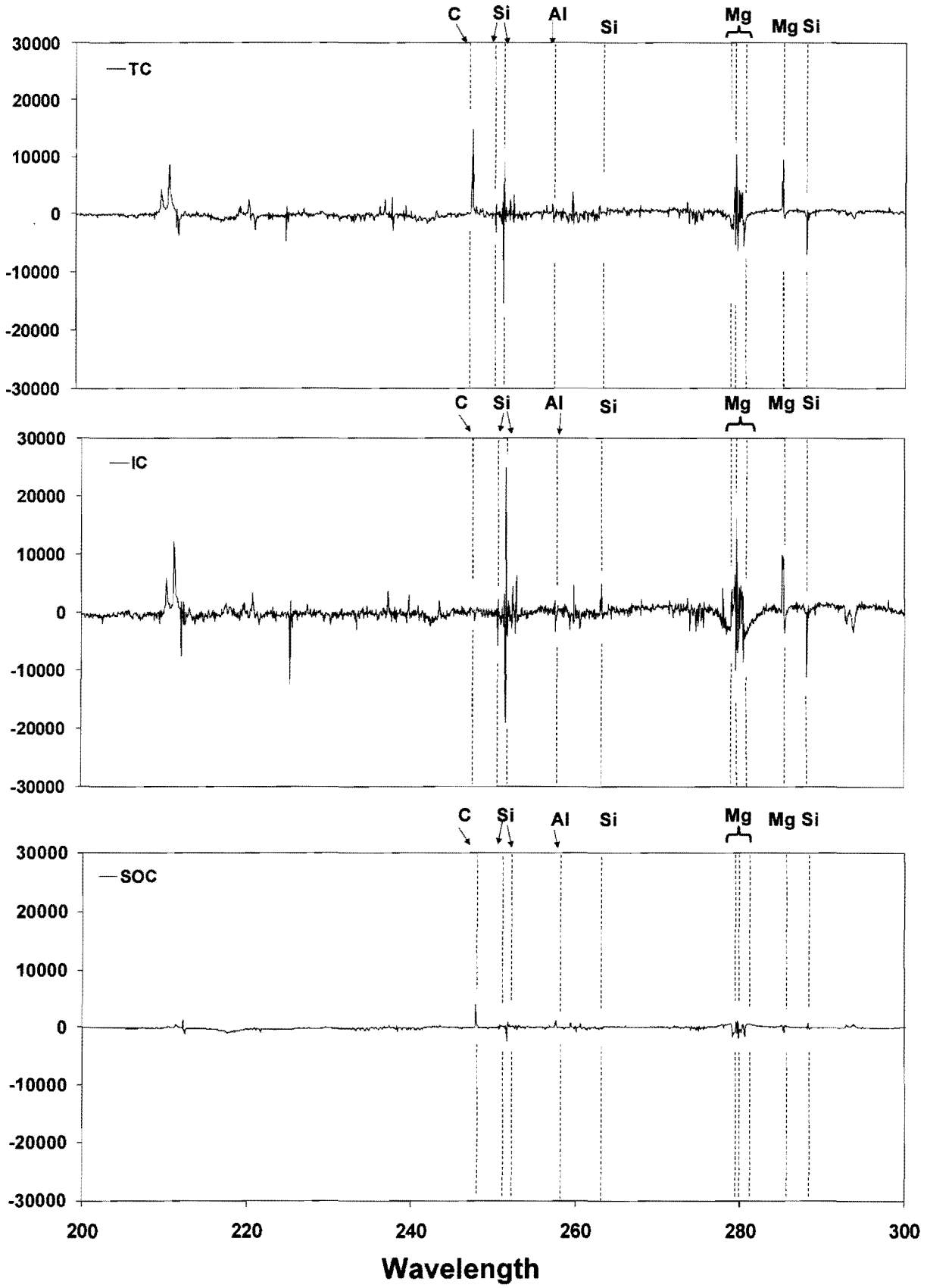
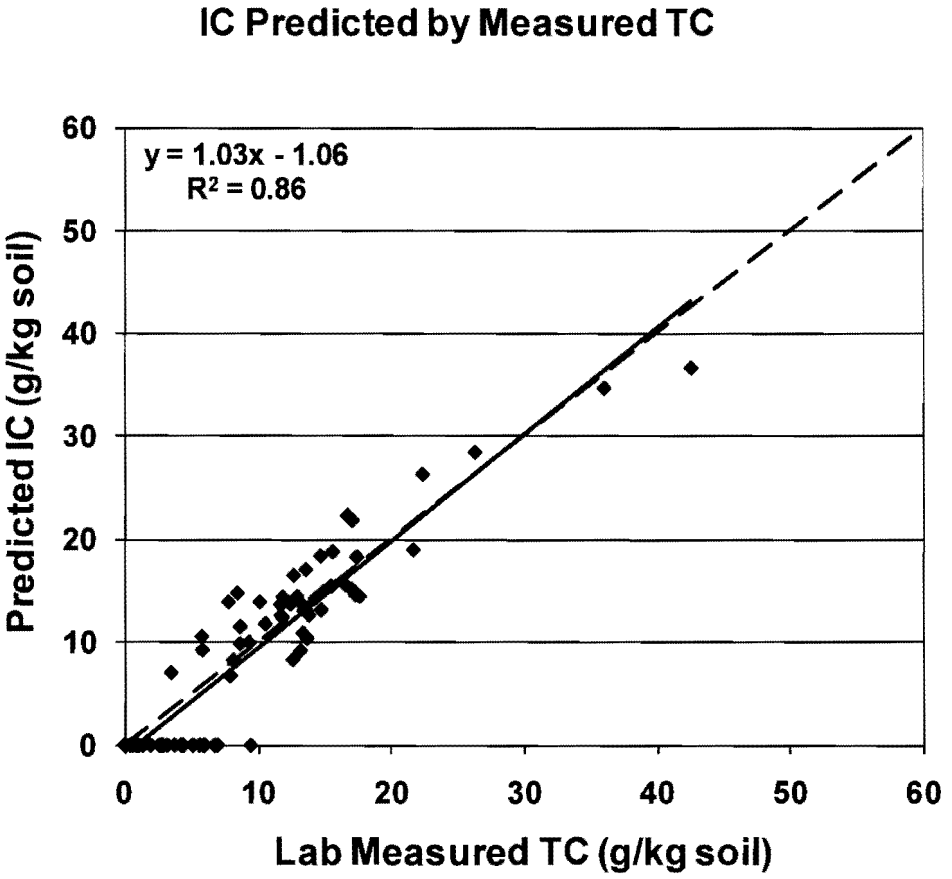


Figure 3. Partial least squares regression (PLSR) coefficients for soil total, inorganic, and organic carbon. The magnitude of the coefficients indicates the relative importance of each emission line. Dashed vertical lines indicate important elemental emission lines for predicting the various forms of soil carbon.

562 **Figure 4.**



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566 a large portion of total C in these semi-arid glacial till soils.

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Figure 5.

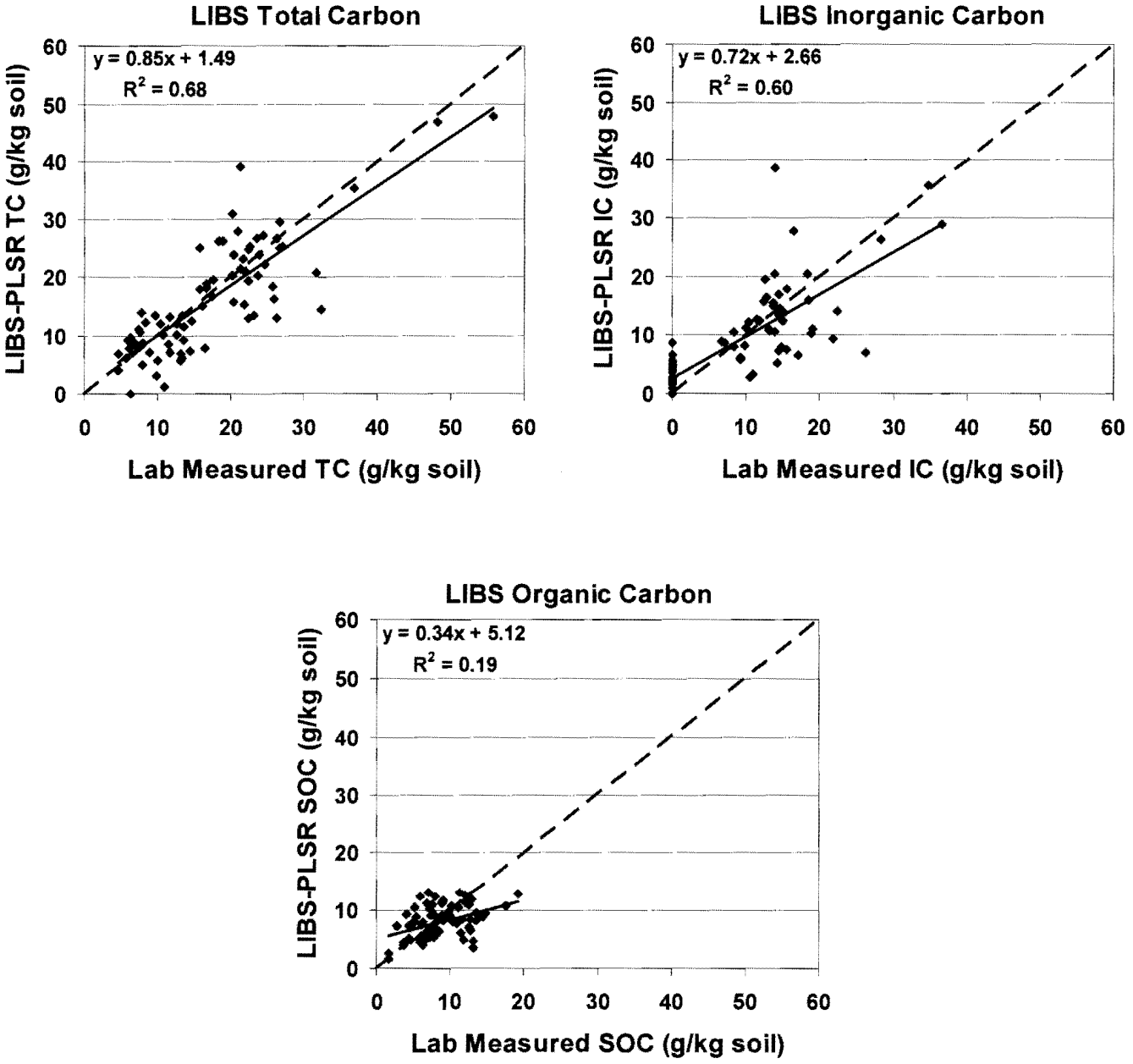

Figure 5. Independent validation of predicted soil total carbon (TC), inorganic carbon (IC), and organic carbon (SOC) using LIBS and partial least squares regression models. Nine interrogation spectra were averaged for PLSR analysis.

608 **Figure 6**

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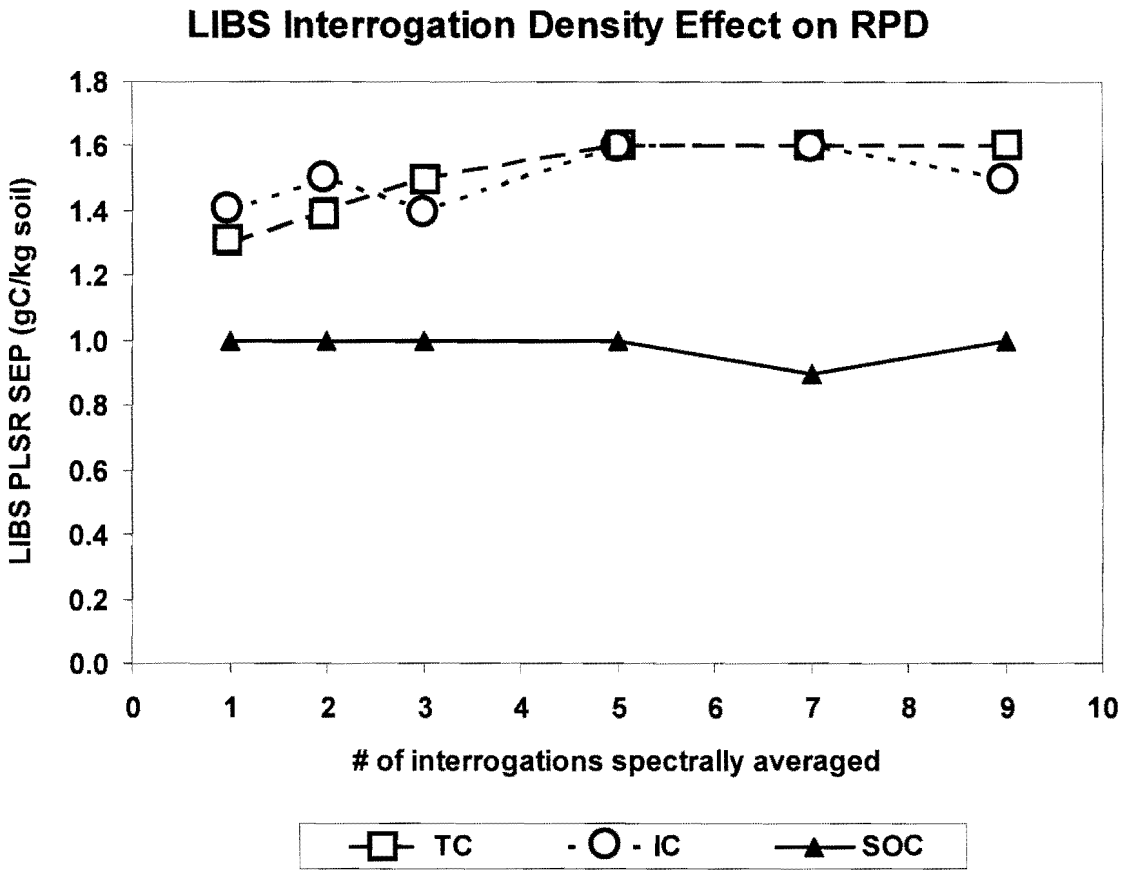

Figure 6. Predictive accuracy response, as indicated by the Residual Product Differential (RPD), to spectrally averaging multiple LIBS interrogation points for soil total carbon (TC), inorganic carbon (IC), and organic carbon (SOC) determination.