In Situ Measurements of Soil Carbon with Advanced Technologies

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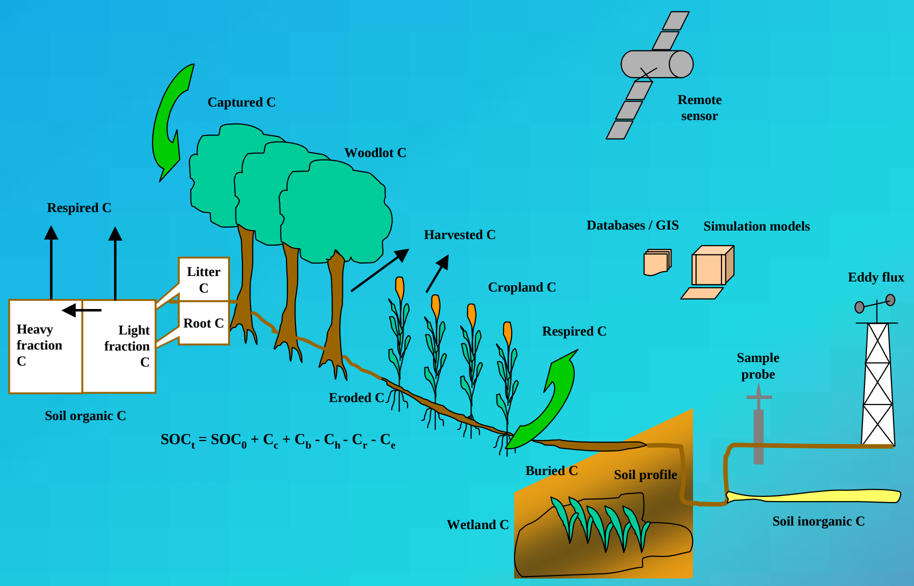
Introduction and Objective

- Changes in soil C stocks can be measured directly through soil sampling or estimated using stratified accounting, or simulation models
- Steps for measuring soil C include soil sampling, sample preparation, measurement by dry combustion, and calculation of results on a soil-mass basis
- However, there is a need to develop fast and accurate procedures to measure soil C changes at the field scale
- The objective of this research, supported by NRCS and USAID, was to evaluate the performance of advanced technologies in their ability to measure soil



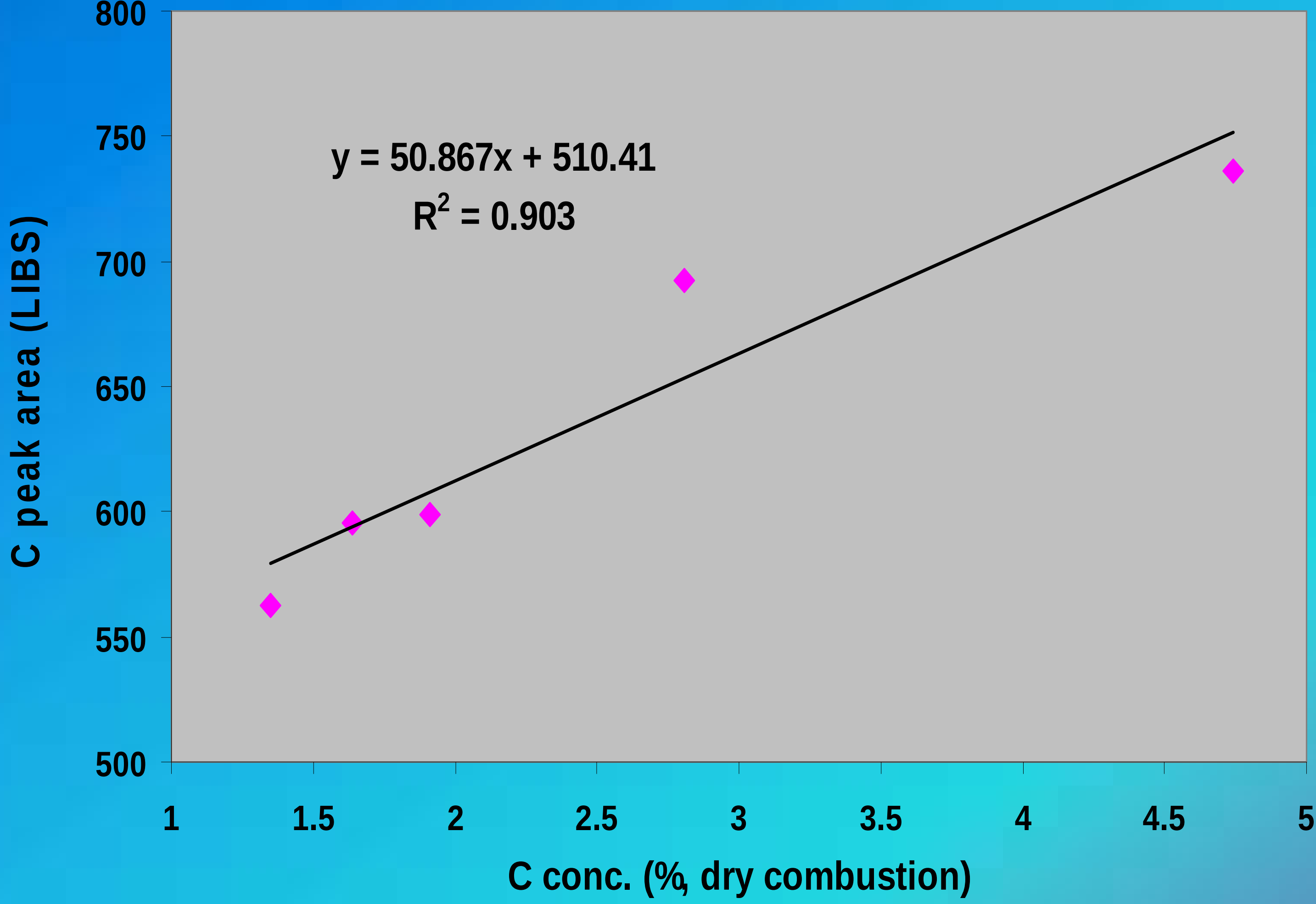
Post et al. (2001) Climatic Change 51:73-99

Laser Induced Breakdown Spectroscopy: LIBS

- Based on atomic emission spectroscopy
- Portable
- A laser pulse is focused on a soil sample, creating high temperatures and electric fields that break all chemical bonds and generating a white-hot plasma
- The spectrum generated contains atomic emission peaks at wavelengths characteristic of the sample's constituent elements

Cremers et al. (2001) J. Environ. Qual. 30:2202-2206

Fig. 1. Regression analysis of C concentration by dry-combustion (DC) and LIBS peak area



Carbon measurement by LIBS

Soil ID	N	C conc. (%) Mean	Std Dev	Minimum (%)	Maximum (%)
1F	4	1.04	0.17	0.80	1.19
2F	4	1.66	0.57	1.15	2.43
3F	4	4.32	0.30	3.91	4.57
4F	4	3.48	0.47	2.95	3.99
5F	4	1.66	0.19	1.52	1.93

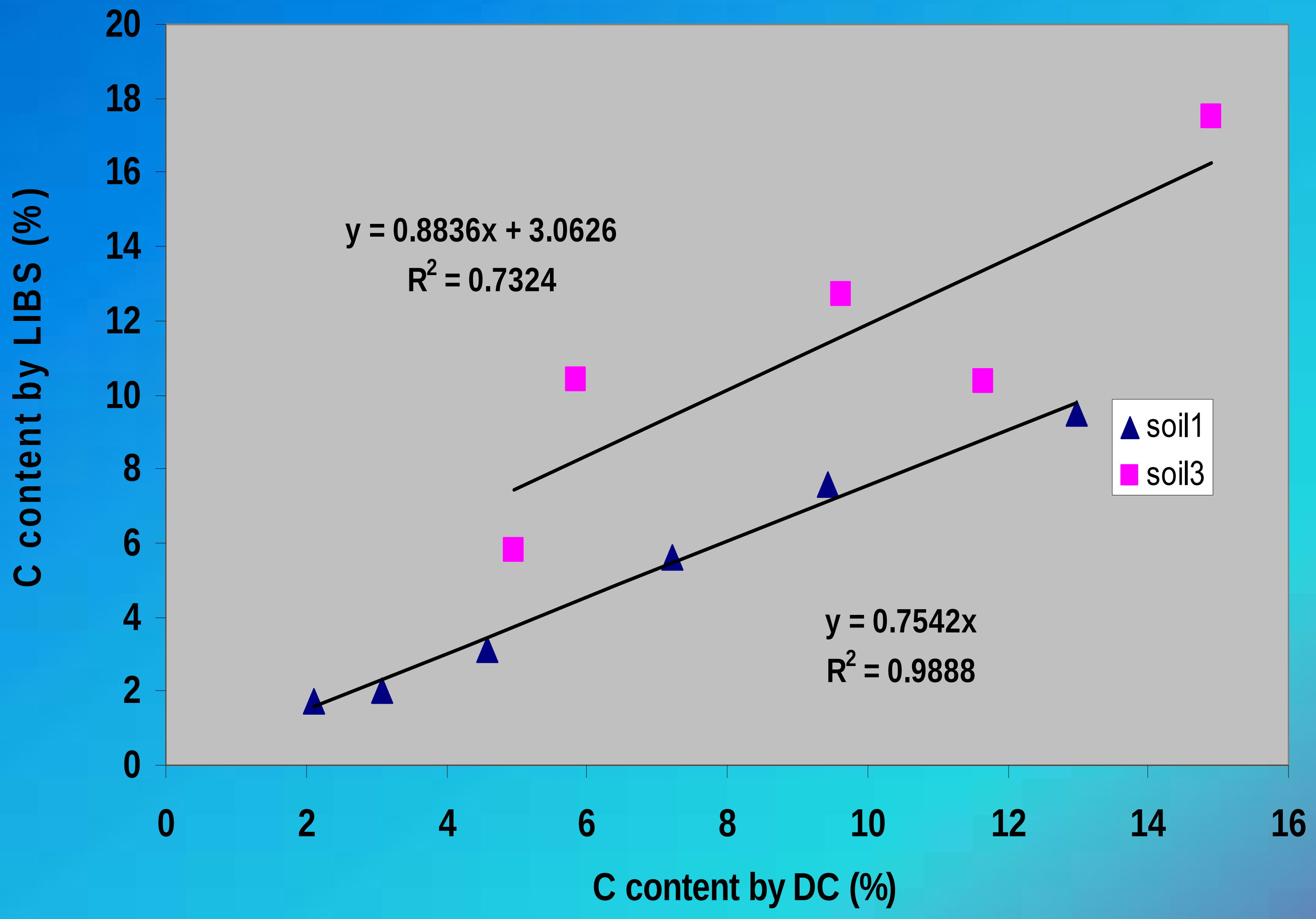
Organic Carbon Recovery by LIBS

Soil ID	C conc. (%) (DC)	C conc. (%) (LIBS)	Recovery Rate (%)
T6	2.12	1.71	81
T5	3.09	2.00	65
T4	4.59	3.14	68
T3	7.21	5.61	78
T2	9.43	7.60	81
T1	12.98	9.52	73

Organic Carbon Recovery by LIBS

Soil ID	C conc. (%) (DC)	C conc. (%) (LIBS)	Recovery Rate (%)
T12	4.96	5.83	117
T11	5.85	10.42	178
T9	9.63	12.71	132
T8	11.66	10.37	89
T7	14.91	17.52	117

Fig. 5. Organic C Recovery



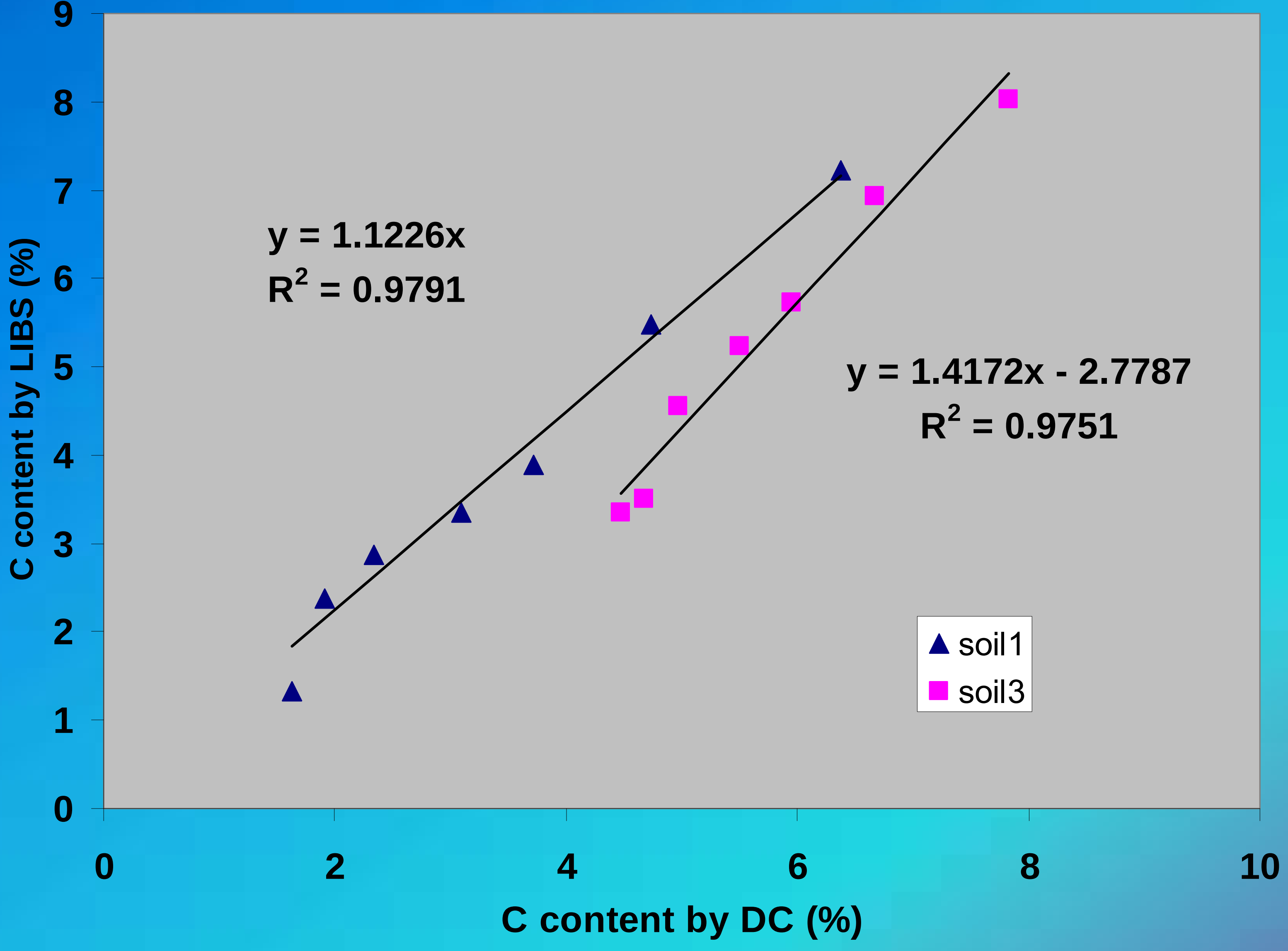
Inorganic Carbon Recovery by LIBS

Soil ID	C conc. (%) (DC)	C conc. (%) (LIBS)	Recovery Rate (%)
T19	1.63	1.33	82
T18	1.91	2.38	125
T17	2.34	2.87	123
T16	3.09	3.34	108
T15	3.72	3.89	105
T13	4.73	5.48	116
T12	6.38	7.22	113

Inorganic Carbon Recovery by LIBS

Soil ID	C conc. (%) (DC)	C conc. (%) (LIBS)	Recovery Rate (%)
T26	4.48	3.35	75
T25	4.67	3.51	75
T24	4.97	4.56	92
T23	5.50	5.24	95
T22	5.95	5.72	96
T21	6.67	6.93	104
T20	7.83	8.03	103

Fig. 6. Inorganic C Recovery



Inelastic Neutron Scattering: INS

- Non-invasive technique that consists in directing fast neutrons (14 MeV) produced by a neutron generator into the soil, where they interact with the nuclei of atoms of various elements, including ^{12}C
- Fast neutrons collide with ^{12}C atoms and release energy (4.4 MeV) as γ ray photons
- Stationary and a scanning versions of the INS were tested
- Soil mass interrogated: >200 kg

Wielopolski et al. (2000) IEEE Trans. Nuclear Sci. 47:914-917

Mid-Infrared Reflectance Spectroscopy: MIRS

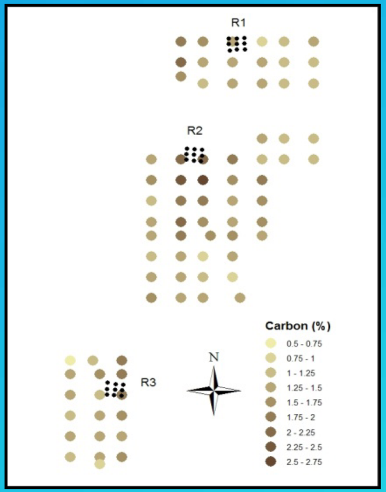
- Unlike LIBS and INS, MIRS probes the bond identities of a sample's molecules, offering the possibility of directly distinguishing inorganic from organic C, thus eliminating the need for acid pretreatment to remove inorganic C

- Quantifying soil C must be done indirectly, by recourse of advanced data-fitting routines that require libraries of soil spectra vs. soil C data

McCarty et al. (2002) Soil Sci. Soc. Am. J. 66:640-646

First Field Test: Beltsville, MD; October 2006

- Three 30 m x 30 m plots containing 9 sampling points were sampled at three depth intervals (0-5, 5-15, 15-30 cm)
- Soil samples were processed in the field for LIBS and MIRS analysis
- The INS instrument estimated soil C density via soil scanning
- All samples were analyzed for C content at Kansas State Univ. by dry combustion and the results reported as soil C density using D_b determined by the soil core method



Mean soil C density (g C cm^{-2}) to a depth of 30 cm

- A subset of C concentration values determined by dry combustion (DC) was provided to all teams
- MIRS produced the closest estimates of soil C density but required the largest amount of information
- LIBS estimates could be improved by including more data points into the universal calibration curve
- INS estimates should be further explored with regards to uncertainties:
  - True mean soil C density value was lower than the estimated by the DC and soil sampling
  - Inaccurate soil bulk density determinations
  - Inaccurate estimation of soil volume and especially soil depth by the INS instrument

	DC	LIBS	INS	MIRS
μ	0.407	0.327	0.257	0.432
σ	0.055	0.081	0.052	0.061
n	9	9	-	9
%Diff		-20	-37	+6

Re-visiting Plot with INS to estimate soil C density (g C cm^{-2})

- The two repeated INS measurements gave similar values (μ_{INS} = 0.257 g C cm^{-2}) but the mean value was different from that determined by DC (μ_{DC} = 0.407 g C cm^{-2})
- Two hypotheses are possible:
  - The true mean soil C density of the field is lower than predicted from a finite number of grid points
  - The INS calibration was based on too few points; thus, more calibration points are needed to improve the prediction of soil C density

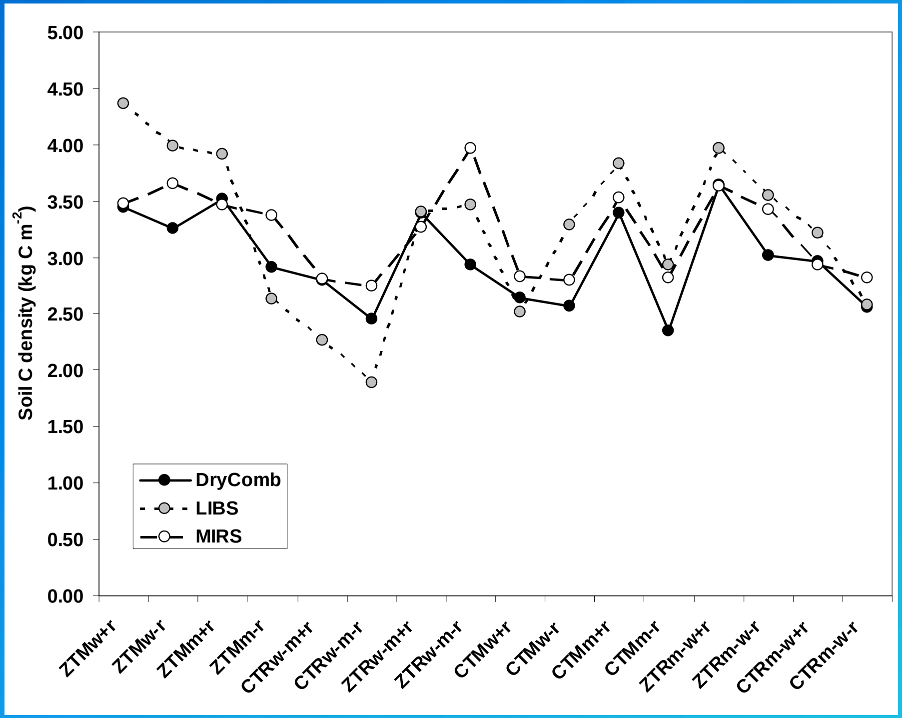
	Static Meas.	Scanning	Dry Comb.
Visit I	0.388	0.252	0.407
Visit II	0.392	0.262	0.407

Wielopolski et al. J. Environ. Qual. (accepted for public.)

Second Field Test: CIMMYT, Mexico; April 2007

- Conducted at CIMMYT on a 17-year old crop rotation, tillage, residue study
- Treatments sampled:
  - Maize (m) and wheat (w) grown in monoculture (M) or in rotation (R)
  - Grown with conventional (CT) or no tillage (ZT), and with (+) or without (-) removal of crop residues
  - Each treatment is replicated twice
- A composite soil sample made of 12 subsamples per soil depth (0-5, 5-10, and 10-20 cm) was taken from each of the 22 x 7.5 m plots
- Soil samples were processed and analyzed as in the Beltsville test. This test did not include the INS instrument

Mean soil C density (kg C m^{-2}) by treatment and summary statistics in the CIMMYT experiment

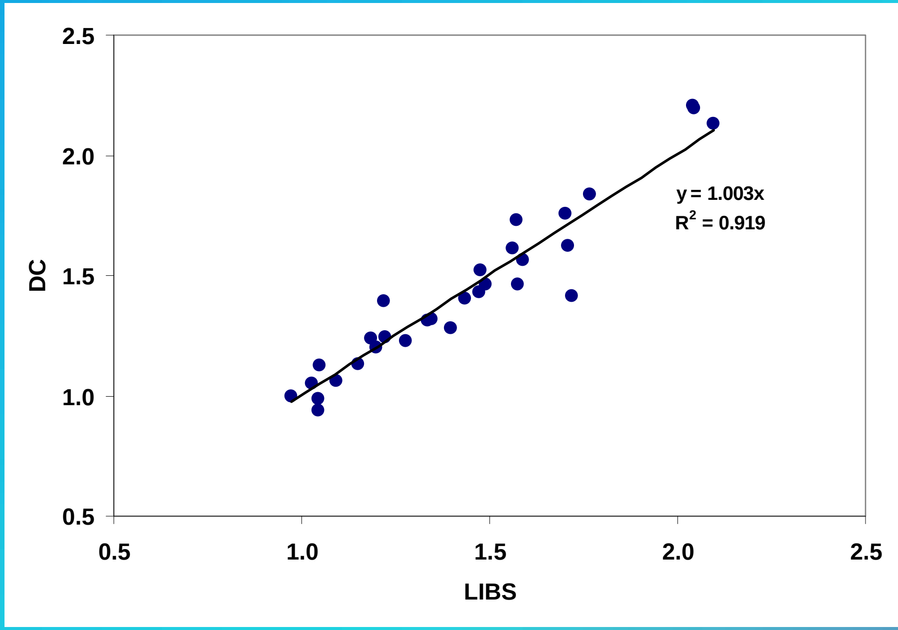


- LIBS and MIRS followed the C density trends detected by DC method
- Correlation between methods was low
  - LIBS vs. DC: $R^2 = 0.174$
  - MIRS vs. DC: $R^2 = 0.329$

	DC	LIBS	MIRS
μ	1.306	1.440	1.413
σ	0.301	0.393	0.134
Max	2.315	2.300	1.791
Min	0.814	0.600	1.166
Range	1.500	1.700	0.625
n	112	112	112

Further calibration of LIBS and re-estimation of CIMMYT data

- Partial Least Squares method was used to improve calibration curves
- A calibration curve was developed using 31 samples run 3 times each (1 missing value)
- Re-estimation of data points improved significantly (see graph on the right)
- Software issues need to be addressed by Australian developers
- New software (The Unscrambler), is being tested



Further calibration of MIRS and re-estimation of CIMMYT data

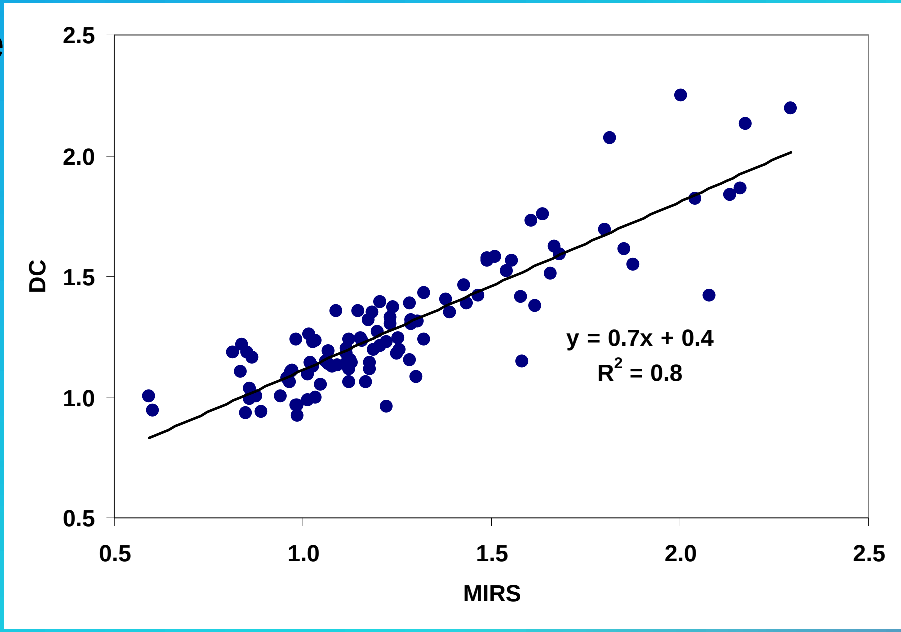
- Original estimation of CIMMYT data using MIRS was developed with the calibration curve based on US samples and 8 samples from Mexico

- Eleven samples from the set of 112 were added to the calibration curve

- Prediction of the remainder 101 points improved significantly with the revised calibration curve that used the US data points plus the 19 Mexico data points

- A calibration using only the 112 samples had high R^2 (~0.95) and revealed nothing wrong with the DC data

- With the MIRS method, the greatest difficulty in predicting the correct values seems to be associated with high C samples



Summary

- This study compared the side-by-side performance of three advanced technologies to measure soil C under field conditions: LIBS, INS, and MIRS
- The LIBS and MIRS results compare directly with those obtained by dry combustion. These methods require soil sampling and need soil bulk density information to convert soil C concentrations to soil C density.
- The INS instrument interrogates large volumes of soil to generate mean soil C values for the site measured or field scanned. The INS requires calibration with mean values obtained from soil sampling measurements. Comparison between INS and discrete soil sampling measurements requires further study.
- The results obtained indicate acceptable performances of the advanced instruments but they also show the need for improvement in terms of calibration.
- The three instruments demonstrated their portability and their capacity to perform under field conditions.

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