Comparison of Soil Carbon Measuring Techniques

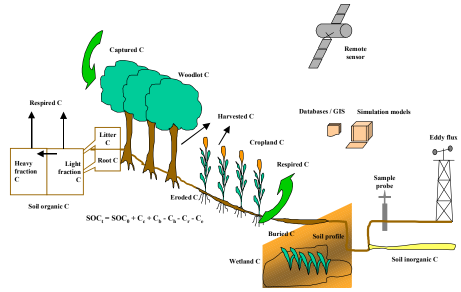
R.C. Izaurralde, M.H. Ebinger, J.B. Reeves, C.W. Rice,
L. Wielopolski, B.A. Francis, R.D. Harris, S. Mitra,
A.M. Thomson, J.D. Etchevers, K.D. Sayre,
A. Rappaport, and B. Govaerts

Agriculture's Role in the New Carbon Economy
CASMGS Forum

Manhattan, KS
17-18 December, 2007

Introduction

- Changes in soil C stocks can be measured directly through soil sampling or estimated using eddy covariance, 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



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

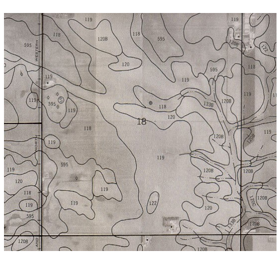
Objectives

- Discuss issues related to the detection of soil C changes as a result of changes in agricultural management
- Compare the performance of three advanced technologies in their ability to measure soil C under field conditions and use in developing countries:
  - Laser Induced Breakdown Spectroscopy: LIBS
  - Inelastic Breakdown Spectroscopy: INS
  - Mid-Infrared Reflectance Spectroscopy: MIRS

3

Measuring and monitoring soil C sequestration: a new challenge?

Long term experiments have been essential tools to understand the temporal dynamics of soil C

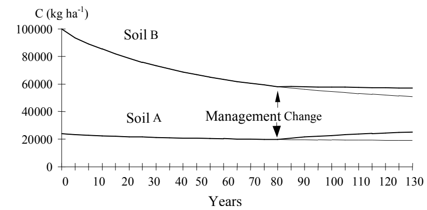


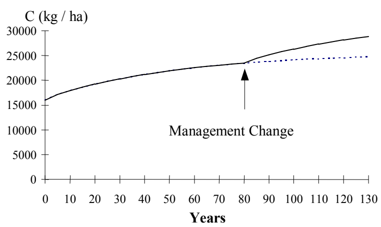
Soil survey maps can be used to estimate the spatial distribution of soil organic C stocks

The challenge consists in developing cost-effective methods for detecting changes in soil organic C that occur in fields as a result of changes in management

On baselines, soil C sequestration and avoided C loss

Soils with different C stocks may respond differently to changes in management



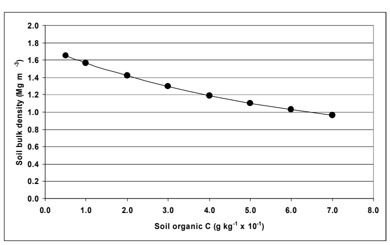


Time 0 baseline in a soil gaining C may lead to an overestimation of soil C sequestration

McGill et al. (1996)

5

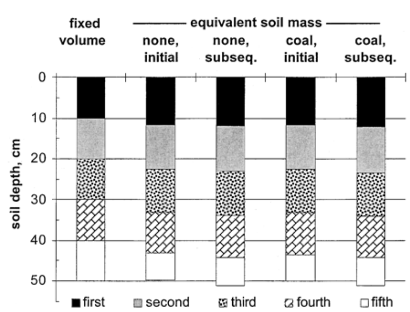
Soil organic matter affects soil bulk density and thus temporal comparisons of soil C stocks



Soil bulk density is a function of the soil mineral density and the soil organic matter content

$$\rho_b = \frac{100}{\frac{\%OM}{0.244} + \frac{100 - \%OM}{\rho_m}}$$

Comparisons of soil C stocks across treatments should be done using the equivalent soil mass method

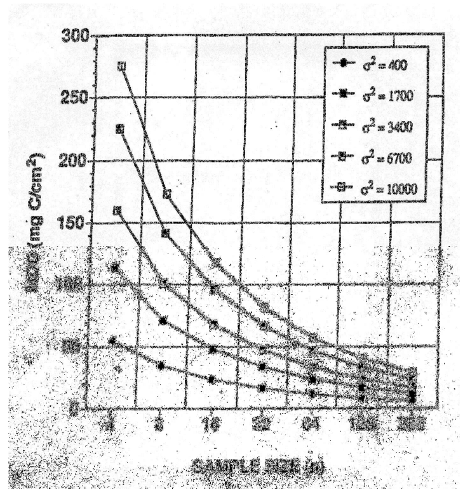


Ellert et al. (2002)

6

Spatial variability influences estimates of soil organic C

- 100 samples to detect 2-3% change in SOC
- 16 samples to detect 10-15 % change in SOC

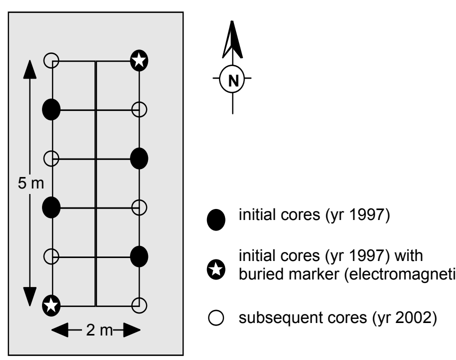


Garten and Wullschleger (1999)

7

Sampling protocol used in the Prairie Soil Carbon Balance (PSCB) project

- Use “microsites” (4 x 7 m) to reduce spatial variability
- Three to six microsites per field
- Calculate SOC storage on an equivalent mass basis
- Analyze samples taken at different times together
- Soil C changes detected in 3 yr
  - 0.71 Mg C ha^{-1} – semiarid
  - 1.25 Mg C ha^{-1} – subhumid



Ellert et al. (2001)

8

Grid and sampling schemes demonstrate that soil C stocks can be determined with low errors

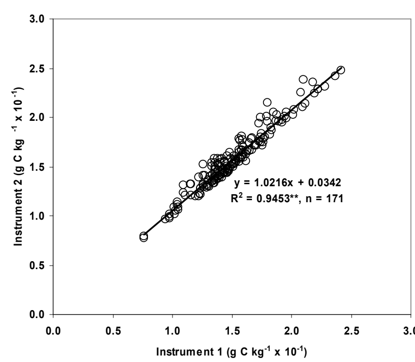
Soil C (Mg C ha^{-1} to 30-cm soil depth)

	Mean	SD	CV	n
Grid 1	48.4	3.9	8.0	25
Grid 2	47.8	3.5	7.4	25
Grid 3	47.8	2.7	5.7	25
Average	48.0	3.4	7.0	75
Comp 1	48.5			1
Comp 2	44.7			1
Comp 3	46.7			1
Average	46.6	1.9	4.1	3

Source: G. Watson and C. Rice 9

Determination of soil organic C concentration: standard methods

- Wet combustion
  - Soil sample treated with acid dichromate solution
  - CO_2 generated evaluated with titrimetric or gravimetric methods
  - Recovery is incomplete (avg. 81%)
- Dry combustion
  - High temperature (1000 – 1500 C)
  - CO_2 generated assessed with spectrophotometric, volumetric, titrimetric, gravimetric, or conductimetric techniques
  - Very accurate, minimal variability, low operational errors
  - Corrections needed when samples contain carbonates
- National and international efforts needed to cross-calibrate methods against standard (soil) samples



Total soil C as measured by two dry combustion instruments

Izaurralde and Rice (2006)

10

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
- A calibration curve is required to predict soil C concentration

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

Inelastic Neutron Scattering: INS

- *In situ, non-destructive* 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 including ^{12}C and other atoms (H, N, O, Si, K, Ca, P, etc.)
- Fast neutrons collide with C, H, and N atoms and release gamma rays with energies of 4.4, 2.2, and 10.3 MeV
- Soil mass interrogated: >200 kg
- The INS was tested in stationary and scanning modes

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

The INS in action…

13

Mid-Infrared Reflectance Spectroscopy: MIRS

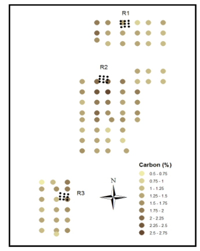
- Unlike LIBS and INS, MIRS probes the bond identities of a sample's molecules, offering the possibility of directly distinguishing inorganic from organic C, thus eliminating the need for acid pretreatment to remove inorganic C
- Yet for the same reason, quantifying soil C must be done indirectly, by 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

14

First Field Test: Beltsville, MD; October 2006

- Conducted on a 25-ha field known as OPE3 (Optimizing Production Inputs for Economic and Environmental Enhancement)
- 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
- The dry-combustion team provided selected C values to the other teams for calibration and then collected the C estimates for Plot No. 3 (R3) from the other teams for comparison



15

Mean soil C density (g C cm^{-2}) to a depth of 30 cm in Plot No. 3 of OPE3 field

- A subset of C concentration values determined by dry combustion (DC) was provided to all teams
- Soil C density estimates for Plot No. 3 are the results of a blind test
- 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:
  - Calibration procedures
  - Variability of soil C density

	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

16

Re-visiting Plot No. 3 of OPE3 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 of the Plot No. 3 of the OPE3 field

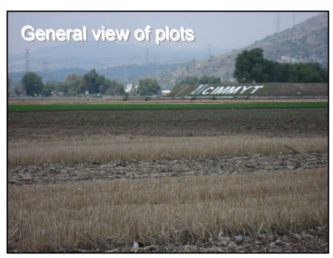
	Static Meas.	Scanning	Dry Comb.
Visit I	0.388	0.252	0.407
Visit II	0.392	0.262	0.407

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

17

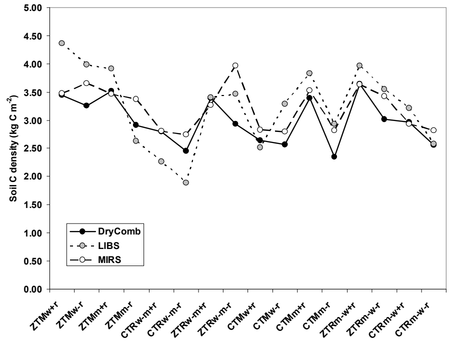
Second Field Test: CIMMYT, Mexico; April 2007

- This test did not include the INS instrument
- 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.



18

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



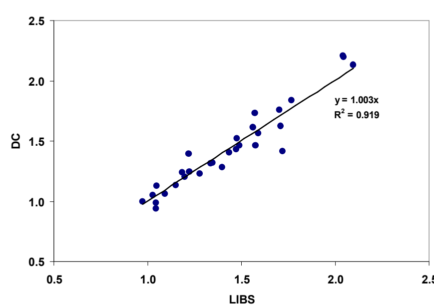
- Although LIBS and MIRS followed the C density trends detected by DC method
- Correlation between methods was low
  - LIBS vs. DC: $R^2 = 0.174$
  - MIRS vs. DC: $R^2 = 0.329$

	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

19

Further calibration of LIBS and re-estimation of CIMMYT data

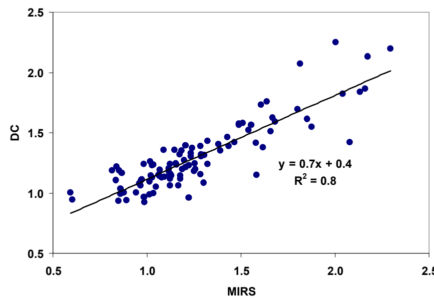
- Partial Least Squares method was used to improve calibration curves
- A calibration curve was developed using 31 samples run 3 times each (1 missing value)
- Re-estimation of data points improved significantly (see graph on the right)
- Software issues need to be addressed by Australian developers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



20

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 OPE3 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 OPE3 data points plus the 19 Mexican data points
- With the MIRS method, the greatest difficulty in predicting the correct values seems to be associated with high C samples
- A calibration using only the 112 samples had high R^2 (~0.95) and revealed nothing wrong with the DC data
  - Recently, the Colegio de Postgraduados (CP) in Texcoco (Mexico) ran dry combustion in all of the soil samples
  - The R^2 between CP and KSU data was >0.9



Summary

- This study compared for the first time 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 Comb. 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 measurements require 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
- Import / export issues to developing countries should be examined in order to facilitate the transport of these instruments across international borders