

# Measuring Total Carbon and Nitrogen in Soils Using Laser-Induced Breakdown Spectroscopy (LIBS)

R. D. Harris<sup>1</sup>, M. H. Ebinger<sup>1</sup>, C. W. Meyer<sup>1</sup> and R. J. Gehl<sup>2</sup>

<sup>1</sup> Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545

<sup>2</sup> Department of Agronomy, Kansas State University, Manhattan, KS 66506

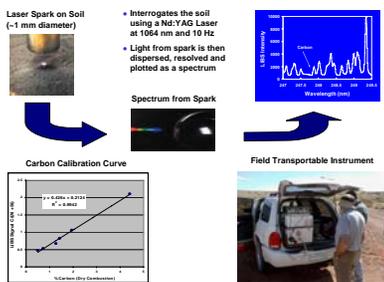
## Introduction

Loss of soil carbon during the past 150 years has depleted many of the most productive soils and resulted in degradation of marginal soils. The potential to restore carbon stocks in different landscapes through careful land management practices could result in significant improvements to crop production in agricultural lands and overall soil quality improvements in other lands (Lal, 2004; IPCC, 2000). Increases in soil organic carbon (SOC) depend on climate and management practices, with potential increases estimated from 0 to 150 kg C ha<sup>-1</sup> yr<sup>-1</sup> in semiarid environments and up to 1000 kg C ha<sup>-1</sup> yr<sup>-1</sup> in more humid environments (Lal, 2004; Armstrong et al., 2003; West and Post, 2002). Existing methods of carbon analysis (e.g., Rossel et al., 2001; Scharpenseel et al., 2001) provide the analytical tools needed to estimate these increases in the SOC pool with some precision.

Advanced analytical methods (e.g., Ebinger et al., 2003; McCarty et al., 2002; McCarty and Reeves, 2001; Cremers et al., 2001) offer improved detection, ease of operation, and potential use in the field that improve precision and accuracy of SOC measurements. In addition, the need for improved accuracy and precision to support national and international policies on carbon emissions and carbon trading may require orders of magnitude more measurements to provide valid support for various positions and land management practices. These measurements must be delivered at the lowest cost possible and with well characterized uncertainties. Existing methods fall short on cost effectiveness as well as accuracy and precision; advanced methods, once fully developed and tested, will optimize the amount of information about SOC pools per dollar spent, and will be designed to keep the cost of assessing carbon to less than 10% of the total costs of sequestration practices (DOE, 2004). With sequestered carbon becoming a commodity in the United States and Europe, there is the growing need to measure and certify SOC within 3 to 5 years of implementing carbon sequestration and management practices and to do so with the greatest levels of precision and accuracy.

Developing cost effective and rapid methods of measuring soil carbon is important to address aspects of global climate change and terrestrial carbon management issues. Over the past two decades, several advanced analytical methods have been applied to the study of soil carbon. The detection of nitrogen in soils along with other elements including potassium, phosphorus and sulfur are also of interest to precision farming implementation. Here we present results using laser-induced breakdown spectroscopy (LIBS) for soil core analysis of carbon and initial results of nitrogen quantification in a soil-like matrix.

Fig. 1 Laser-Induced Breakdown Spectroscopy

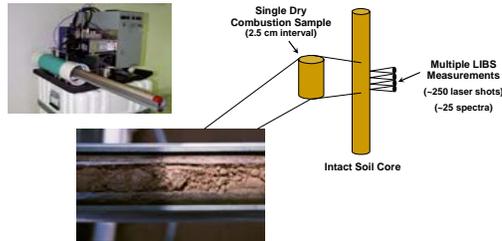


## Methods

A laser is focused on a solid sample and forms a microplasma as the sample is ionized. The light from the microplasma is characteristic of the elemental composition of the sample. This emitted light is collected, spectrally resolved, and detected to monitor concentrations of elements via their unique spectral signatures (Fig. 1). When calibrated, the method provides quantitative measurements within seconds for most elements in soil including total carbon, nitrogen, potassium, sulfur and phosphorus.

C(I) emission lines at 247.8 nm or 193.1 nm were selected for this calibration study of LIBS (Ebinger et al., 2003; Cremers et al., 2001). Ten to two-hundred laser pulses, or 'shots' were directed onto a sample to complete one measurement. Typical measurement areas for the LIBS analysis are 1 mm<sup>2</sup>/shot and a collection of one measurement took about 10 – 20 seconds. Peak heights or areas from 247 nm or 193 nm were recorded for the carbon emission line chosen and background signals from the spectra were subtracted. This procedure was repeated at least 5 times for each sample. A silicon emission line around 251 nm was also collected and used as an internal standard. Ratios of the carbon to silicon lines from LIBS were compared to results obtained from an elemental Vario MAX CN dry combustion macro elemental analyzer for each soil sample.

Fig. 2 Sampling for High Resolution Carbon Distributions



Analysis of Intact Soil Cores for Carbon

The primary goal of instrument development was to create a new analysis method that could be used in the field or with soil samples directly obtained from the field with no or little additional preparation. A LIBS instrument was designed and constructed to analyze intact cores of soil extracted with a soil probe (up to 1.3 m in length and 3 cm diameter). The instrument contains a track that gradually moves the soil core under the focal point of the laser for subsequent analysis of the entire core length. Typically, 10 laser shots were used to interrogate each 1 mm along the length of the core. Most cores requires less than an hour to scan and these scans provides data with unique high-resolution carbon distributions, a feature that cannot be provided using conventional analysis (Fig. 2).

## Results

Fig. 3 shows the raw LIBS signal (C/Si Ratio) as a function of core depth. Ten spectra were averaged to produce each point (one mm interval) in the plot. The large spike in LIBS intensity at 165 mm is due to a plant root included in the soil core. Dry combustion analyses were performed on each 2.5 cm interval of the core. LIBS data were grouped in each 2.5 cm interval and the geometric mean and standard deviation were determined for each interval resulting in an estimate for carbon from each 2.5 cm interval along the length of the core. Fig. 4 shows the LIBS geometric mean from each 2.5 cm interval plotted with the dry combustion data. The LIBS data agree with the dry combustion data except for the data point at a mean of 5.5 where the maximum dry combustion value (%C) is underestimated because the plant root in this section of the core was excluded from the sample during dry combustion analysis.

Fig. 3 LIBS Raw Data from a 260 mm Core

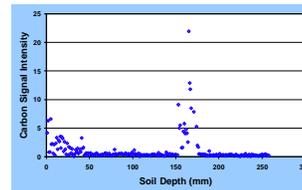


Fig. 4 LIBS Calibration Curve from 260 mm Core

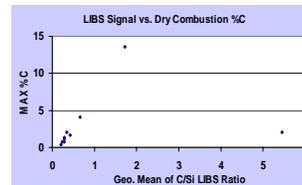
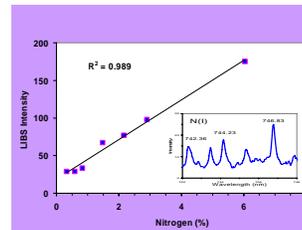


Fig. 5 Nitrogen Calibration Curve from Sand/Clay Mix



## Analysis of Sand/Clay Samples for Nitrogen

The ideal situation for determining nitrogen in soil samples is for measurements to be conducted in air, but this is complicated by the fact that air is 78% nitrogen while nitrogen concentrations in soil are typically < 1%. Discrete samples were made using sea sand, bentonite and Scotts Super Turf Builder (36% N). For the purpose of this experiment a small evacuable chamber was constructed to house the samples so that analysis could be conducted under partial vacuum to reduce atmospheric nitrogen. It was determined that the LIBS signal due to atmospheric nitrogen is negligible at a pressure of 0.04 Torr. Experimental parameters were optimized for the detection of N (I) emission lines at 742.36, 744.23 and 746.83 nm however, the fundamental LIBS instrumentation was the same as that used to quantify carbon in soil cores.

An argon purge can serve as an alternative to the evacuable chamber to allow data acquisition in normal atmospheric pressure. Also, a stream of flowing argon can be used to displace nitrogen (and other gases) on the sample at the location of the laser plasma. Argon gas enhances plasma production and can lower limits of detection for many elements.

## Results

Figure 5 shows a calibration curve for the sand/clay samples ranging from 0.3 to 6% (wt.) in nitrogen. The strongest N (I) emission at 746.83 nm was used for quantifying the nitrogen in the samples though 744.23 nm works as well. Each sample was analyzed 5 times using 100 laser shots. The estimated limit of detection using traditional definitions falls between 0.3 and 0.8% N. Data were acquired using an evacuable chamber at 0.04 Torr. It is believed that an argon gas environment will lower the limit of detection to 0.1 to 0.3% N based on experimental results of other elements in an argon environment.

## Conclusions

- LIBS analyses are field portable and require little to no additional preparation of the samples (Fig. 1-2).
- LIBS analysis of intact cores is a promising new method to provide high resolution carbon distribution data that is not possible with other methods (Figs. 2-4).
- Soil carbon can be analyzed quickly, accurately, and precisely with LIBS as compared to dry combustion (Figs. 3, 4).
- Soil nitrogen can be analyzed in the field with LIBS using a chamber with a partial vacuum or argon purge (Fig. 5).

## References

Amstrong, B. D., S. Miao, N. V. Hobbs, D. J. Basu, and J. Savelly. 2003. Using Zinc, Tin, Potassium, and Legume Residues to Maximize Productivity and Soil Fertility in Opportunity Cropping Systems on Shallow Vertisol. *Soil & Crop Science Society of America* 67:111-120.

Cremers, D. A., M. H. Ebinger, D. S. Brumby, P. J. Umlauf, S. A. Khamisdeh, M. J. Farris, K. M. Cahill, and J. R. Brown. 2001. Measuring Total Soil Carbon With Laser-Induced Breakdown Spectroscopy (LIBS). *J. Environmental Qual.* 30:220-228.

Department of Energy (DOE). 2004. Carbon Sequestration Technology Roadmap and Program Plan-2004. National Energy Technology Laboratory, DOE Office of Fossil Energy Available at: <http://www.osti.gov/energy>. 1-2004.

Ebinger, M. H., M. Lee-Northern, D. S. Brumby, D. A. Cremers, M. J. Farris, P. J. Umlauf, M. S. Lantz, K. L. Gostard and C. W. Meyer. 2003. Extending the Applicability of Laser-Induced Breakdown Spectroscopy for Total Soil Carbon Measurement. *Soil Sci. Soc. Am.* 67:1630-1635.

Harris, R. D., Cremers, D. A., Ebinger, M. H., and Scharpenseel, R. K. 2004. Determination of Nitrogen in Soils Using Laser-Induced Breakdown Spectroscopy. *Appl. Spectrosc.* 58:770-775.

International Panel on Climate Change (IPCC). 2006. Land Use, Land-Use Change, and Forestry. Cambridge University Press.

Lal, R. 2004. Soil Carbon Sequestration Impacts on Global Climate Change and Food Security. *Science* 304:1623-1627.

McCarty, G.W., and J. S. Brown III. 2001. Development of rapid instrumental methods for measuring soil organic carbon. p. 219-263. In: R. Lal et al. (ed.) Assessment methods for soil carbon. Lewis Publ., Boca Raton, FL.

McCarty, G.W., J.B. Flanagan III, V. S. Reesman, R. F. Follett, and M. Stebbins. 2002. Modified soil from Infrared Diffuse Reflectance Spectroscopy for Soil Carbon Measurement. *Soil Sci. Soc. Am. J.* 66:464-468.

Russell, R.A., J.C. Gaborian, and J.A. Gaborian. 2001. Soil organic matter evaluation. p. 311-322. In: R. Lal et al. (ed.) Assessment methods for soil carbon. Lewis Publ., Boca Raton, FL.

Scharpenseel, R., M. H. Ebinger, and P. Becker-Heidmann. 2001. Emission Ratios of N, C, O, and S from LIBS. *Appl. Spectrosc.* 55:1102-1104.

West, T. O., and M. Post. 2002. Soil Organic Carbon Sequestration Rates by Tillage and Crop Rotation. *Soil Sci. Soc. Am. J.* 66:1630.