

Measuring Soil Carbon and Nitrogen Using Laser-Induced Breakdown Spectroscopy (LIBS)

Ronny D. Harris¹, Michael H. Ebinger¹, Clifton W. Meyer¹ and David A. Cremers

¹ Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545,

² SDN Research, 1111 Piedra Rondo, Santa Fe, NM 87501

Introduction

Terrestrial carbon management and sequestration produces a variety of benefits which include reclamation of degraded lands, increased soil productivity, reduced erosion and potentially, slowing carbon dioxide build-up in the atmosphere. 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 practice, with potential increases estimated from 0 to 150 kg-C ha⁻¹ yr⁻¹ in semiarid environments and up to 1000 kg-C ha⁻¹ yr⁻¹ 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).

Developing cost effective and rapid methods of measuring soil carbon is important to address aspects of global climate change and terrestrial carbon management issues. In addition, detection of nitrogen in soils along with other elements including potassium, phosphorus and sulfur are also of interest for increased soil productivity. Here we present results using laser-induced breakdown spectroscopy (LIBS) for soil core analysis of carbon and initial results of the quantification of nitrogen, sulfur and phosphorus in a soil-like matrix.

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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). Ten to two-hundred laser pulses or 'shots' are directed onto a sample to complete one measurement. Typical measurement areas for the LIBS analysis are 1 mm² / shot and a collection of one measurement takes about 10 – 20 seconds. Specific emission lines are chosen to monitor each element of interest. Peak heights or areas are recorded for the each emission line and background signals from the spectra are subtracted. This procedure is repeated at least 5 times for most samples. When calibrated, the method provides quantitative measurements within seconds for most elements in soil including total carbon, nitrogen, potassium, sulfur and phosphorus.

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 (patent pending) 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. The speed of the track is adjustable. Typically, the pulsed laser is operated at 10 Hz (10 laser shots per second). Most cores are analyzed in less than an hour (Fig. 2). C(I) emission lines at 247.85 nm were selected for this calibration study of LIBS (Ebinger et al., 2003; Cremers et al., 2001). A silicon emission line around 251 nm was also integrated and used as an internal standard. After LIBS analysis, soil cores were cut into 2.5 cm sections and each 2.5 cm section of the core was analyzed separately using dry combustion. 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.

Results

Fig. 3 shows the calibration curve derived from plotting the dry combustion analysis of each 2.5 cm core segment with the geometric mean of the LIBS signal (C/Si Ratio) for that 2.5 cm segment. The LIBS data agree with the dry combustion data except for the data point at a LIBS mean of 5.5 % C where the maximum dry combustion value is only 2% C. Here, the dry combustion value is underestimated because a plant root in this section of the core was included for LIBS analysis, but excluded from the sample during dry combustion analysis.

Analysis of Sand/Clay Samples for Nitrogen, Sulfur and Phosphorous

Discrete samples were made and pressed using washed sea sand and bentonite clay as a soil like matrix. Scotts Super Turf Builder (36% N) was added to the soil matrix for nitrogen samples, while Miracle-Gro (30% P₂O₅) was added for phosphorus samples. Sublimed sulfur was used as an additive for sulfur samples. A small evacuable chamber was constructed to house the samples so that analysis could be conducted in a controlled environment. It was determined that a vacuum of 0.04 Torr was sufficient to remove enough atmospheric nitrogen to facilitate soil nitrogen analysis. Experimental parameters were optimized for the detection of N (I) emission lines at 742.36, 744.23 and 746.83 nm. Sulfur samples were analyzed at a reduced pressure of 7 Torr to improve the resolution of the S(II) emission lines at 543.28, 545.38, 547.36, 556.49, 564.00 and 564.70 nm. P(I) emission lines were monitored at 253.40, 253.56, 255.32 and 255.49 nm under normal laboratory conditions for Los Alamos (590 Torr).

Results

Fig. 4 is a nitrogen calibration curve for the sand/clay samples ranging from 0.3 to 6% (wt.) in N. The strongest N(I) emission at 746.83 nm was used for quantifying the nitrogen. Each sample was analyzed 5 times using 100 laser shots. The estimated limit of detection (LOD) using traditional definitions falls between 0.3 and 0.8% N. 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. Fig. 5 is a sulfur calibration curve using samples ranging from 0.5 to 14.9 % (wt.) in S. The S(II) emission at 545.38 nm gave the best results for quantifying the sulfur. Each sample in the calibration curve was analyzed only once using 100 laser shots. The estimated LOD is around 0.01% S. Fig. 6 is a phosphorus calibration curve for samples ranging from 400 to 4300ppm P. Samples were analyzed 5 times using 200 laser shots. The P(I) emission line at 255.32 nm was the only line to produce an adequate calibration curve. The estimated LOD is between 1000 and 2000ppm P.

Conclusions

- LIBS instrumentation for carbon analyses of intact soil cores is field transportable and requires little to no sample preparation (Fig. 1-2).
- Analyses of intact cores agree with dry combustion data and can include large plant roots in the total carbon count (Fig. 3).
- Soil nitrogen, sulfur and phosphorus can be analyzed with LIBS using a sample chamber under a partial vacuum or argon purge and optimizing instrumentation for each specific element (Fig. 4-6).

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Fig. 1 Laser-Induced Breakdown Spectroscopy

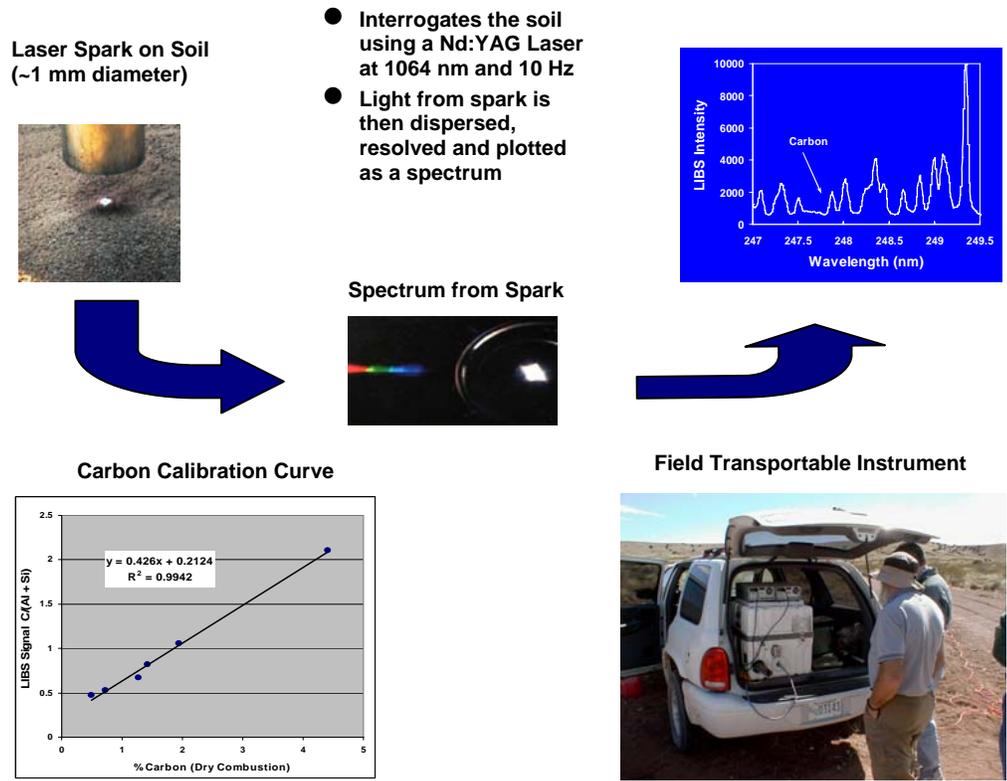


Fig. 2 Sampling of Intact Soil Cores for Carbon

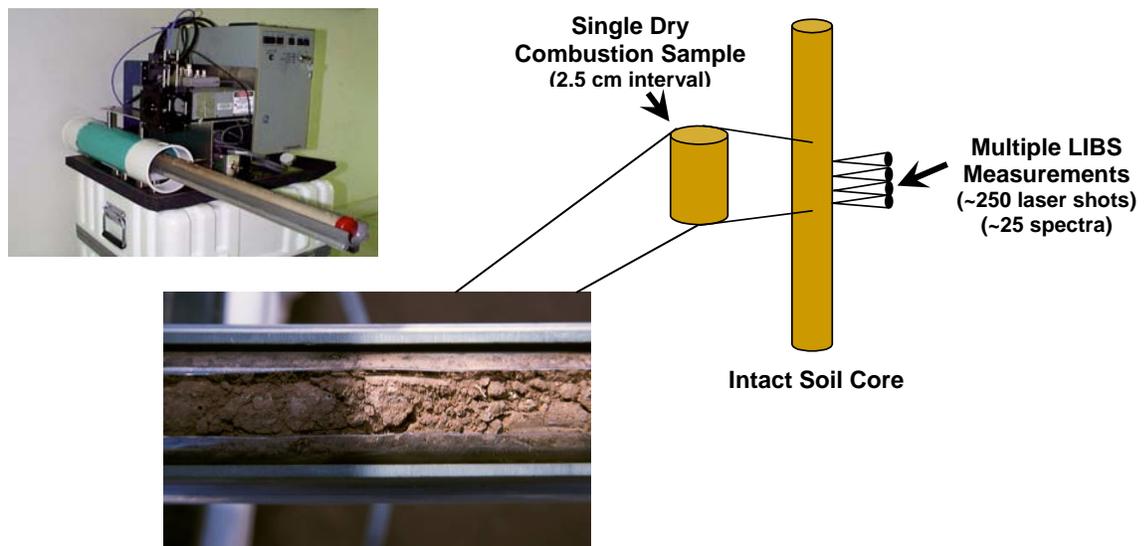


Fig. 3 Carbon Calibration Curve (260 mm Core)

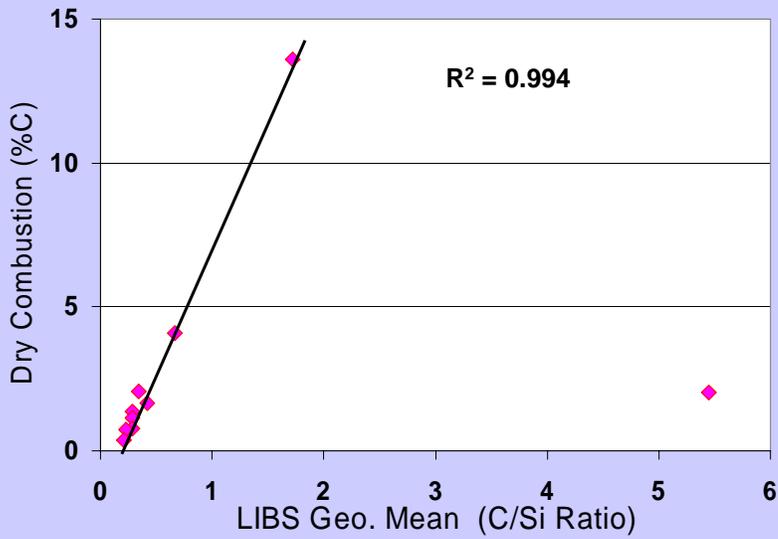


Fig. 4 Nitrogen Calibration Curve (Sand/Clay Mix)

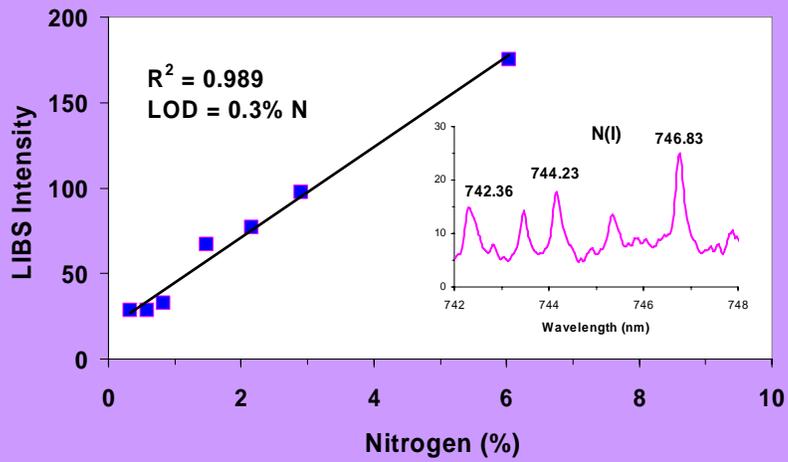


Fig. 5 Sulfur Calibration Curve (Sand/Clay Mix)

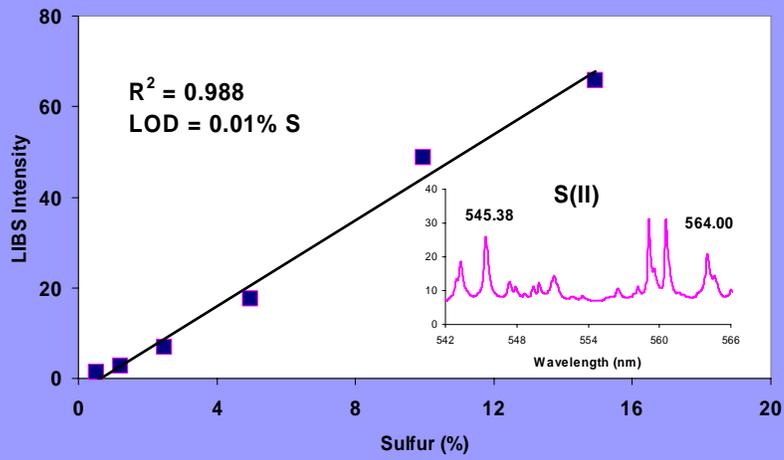


Fig. 6 Phosphorus Calibration Curve and Spectrum

