

Measuring Total Soil Carbon and Other Nutrients Using Laser-Induced Breakdown Spectroscopy (LIBS)

R. D. Harris, P. J. Unkefer, M. H. Ebinger, C. W. Meyer, J. E. Fessenden-Rahn, and S. M. Clegg

Introduction

Developing accurate and rapid methods of measuring soil and plant nutrients is important for increasing soil productivity as well as reducing the costs of precision farming. Loss of soil carbon during the past 150 years has depleted many of the most productive soils and resulted in degradation of marginal soils. Organic matter is needed in soil to provide texture and prevent leaching of other essential nutrients. 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.

In addition to organic matter, thirteen mineral nutrients are needed in the soil for most crops to grow healthy. These consist of the primary macronutrients, nitrogen (N), phosphorus (P) and potassium (K); the secondary macronutrients, calcium (Ca), magnesium (Mg) and sulfur (S); and the micronutrients, boron (B), copper (Cu), iron (Fe), chlorine (Cl), manganese (Mn), molybdenum (Mo) and zinc (Zn). Other elements of interest are nickel (Ni), sodium (Na), vanadium (V), silicon (Si), selenium (Se), barium (Ba), strontium (Sr) and iodine (I), as well as the toxic lead (Pb), arsenic (As), chromium (Cr) and cadmium (Cd).

Here we present results using laser-induced breakdown spectroscopy (LIBS) to analyze soil cores, pressed soil-like samples and pressed plant samples for carbon and mineral nutrients.

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Method

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). Spectrometers and detectors are chosen, depending on the sensitivity and resolution needed for each element. Buffer gases and/or reduced pressures are sometimes used to improve signal and resolution. Ten to two-hundred laser pulses or 'shots' are directed onto a sample to complete one measurement. Typical measurement volumes for the LIBS analysis are 1 mm³ / shot, depending on the sample and laser energy, while 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. This procedure is repeated at least 5 times for most samples. When calibrated, the method provides quantitative measurements within seconds for total carbon and most nutrients including N, K, Ca, P, Mg, S along with some of the micronutrients.

Analysis of Intact Soil Cores for Carbon

The goal of instrument development was to create a field method enabling soil analysis with little or no sample 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 (Fig. 2). The speed of the track is adjustable. The pulsed laser is operated at 10 Hz (10 laser shots per second) with most cores analyzed in less than 30 min. C(I) emission lines at 247.85 nm were selected for this calibration study of LIBS. 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 (elementar Vario MAX CN analyzer). Results of homogeneous cores produce linear correlations with $R^2 = 0.99$ and limit of detections (LOD) better than 0.1 %C. Fig. 3 shows the depth profile of carbon from a specific soil core. Each point was derived by averaging 10 spectra representing ~1 mm of soil core. The peak at ~ 165 mm is due to a piece of tree root contained in the soil core.

Analysis of Pressed 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. P(I) emission lines were monitored at 253.40, 253.56, 255.32 and 255.49 nm under ambient conditions. The P(I) 255.32 nm line produced the calibration curve in Fig. 4. N (I) emission lines were monitored at 742.36, 744.23 and 746.83 nm. The N(I) line at 746.83 nm produced the calibration curve in Fig. 5. S(II) emission lines were monitored between 543.28 and 564.70 nm. The S(II) 543.28 line produced the calibration curve in Fig. 6.

Analysis of Pressed Plant Samples for Nutrients and Other Elements of Interest

Discrete samples of plant leaves (apple, peach, spinach, tomato) and pine needles from NIST-Standard Reference Materials were pressed and analyzed using a Spectrolaser 1000HR (LAT, Bayswater, Victoria, Australia) under ambient conditions. The table below contains limits of detection (LOD) for selected elements. Peaks from carbon, aluminum and silicon are also present in the spectra.

Element	Wavelength (nm)	R²	LOD (ppm)
Ca	865.21	0.986	650
K	766.49	0.975	975
Fe	239.56	0.999	35
Na	588.99	0.763	45
Sr	421.55	0.972	7
Ba	493.41	0.984	35



Conclusions

- **LIBS instrumentation for high resolution depth profiling of carbon in soil cores is field transportable and requires little/no sample preparation (Fig. 1-3). Depth profiling of other elements should be possible.**
- **Soil phosphorus, nitrogen and sulfur can be analyzed with LIBS under specific atmospheric conditions using spectrometers and detectors with appropriate sensitivity (Fig. 4-6).**
- **Calibration curves for calcium, potassium, iron, sodium, strontium and barium in plant leaves were constructed from data collected under ambient conditions using a Spectrolaser 1000HR. Analysis of other elements in plants should be possible using specific conditions for signal enhancement/detection.**

References

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Fig. 1 Laser-Induced Breakdown Spectroscopy

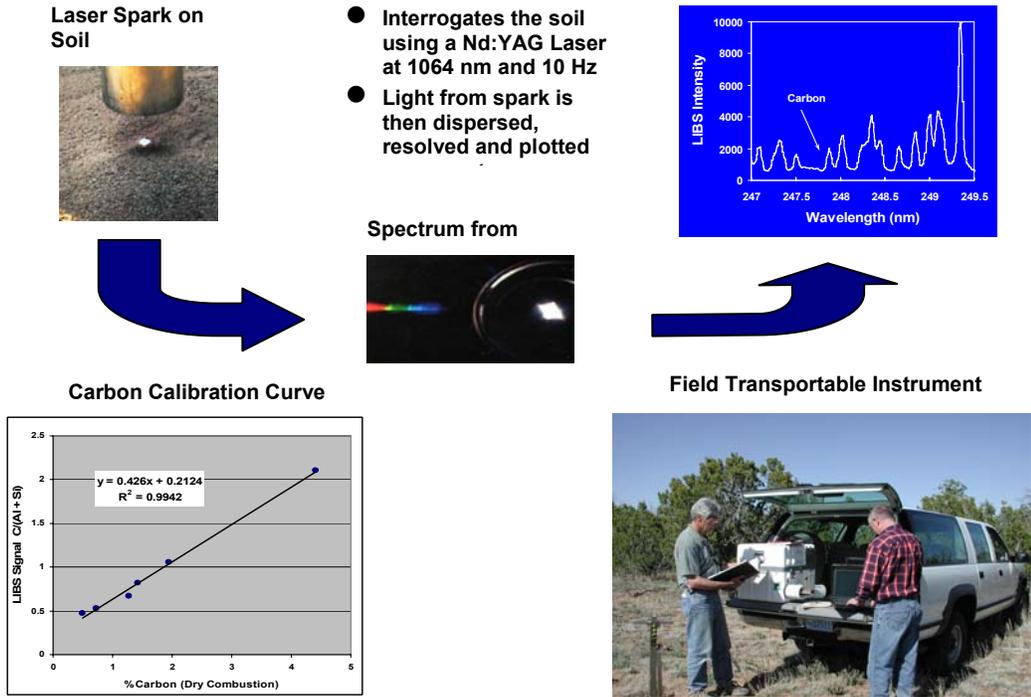


Fig. 2 High Resolution Sampling of Intact Soil Cores for Carbon

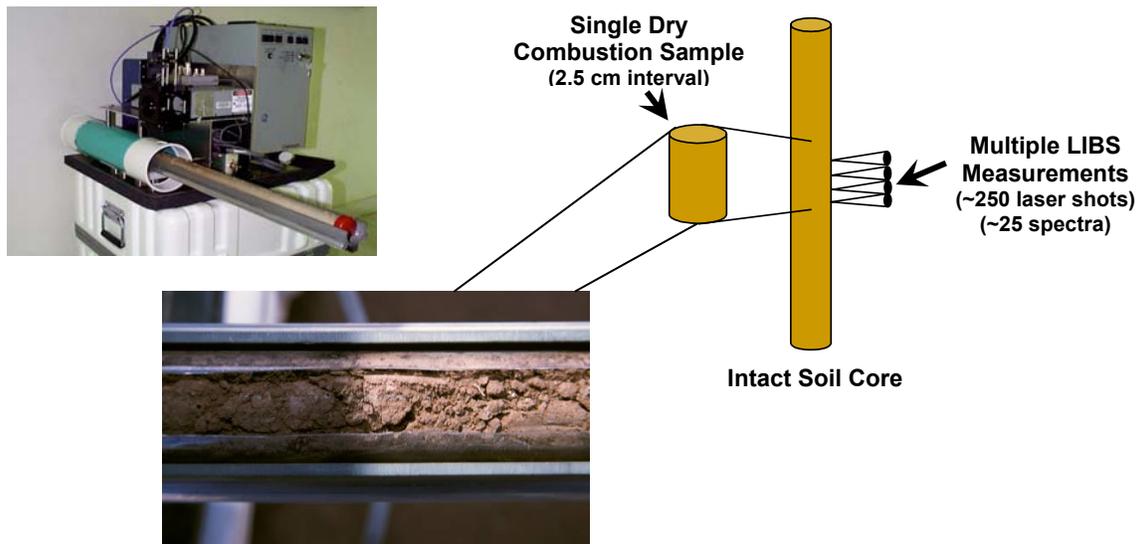


Fig. 3 Depth Profile of Soil Carbon from a Core

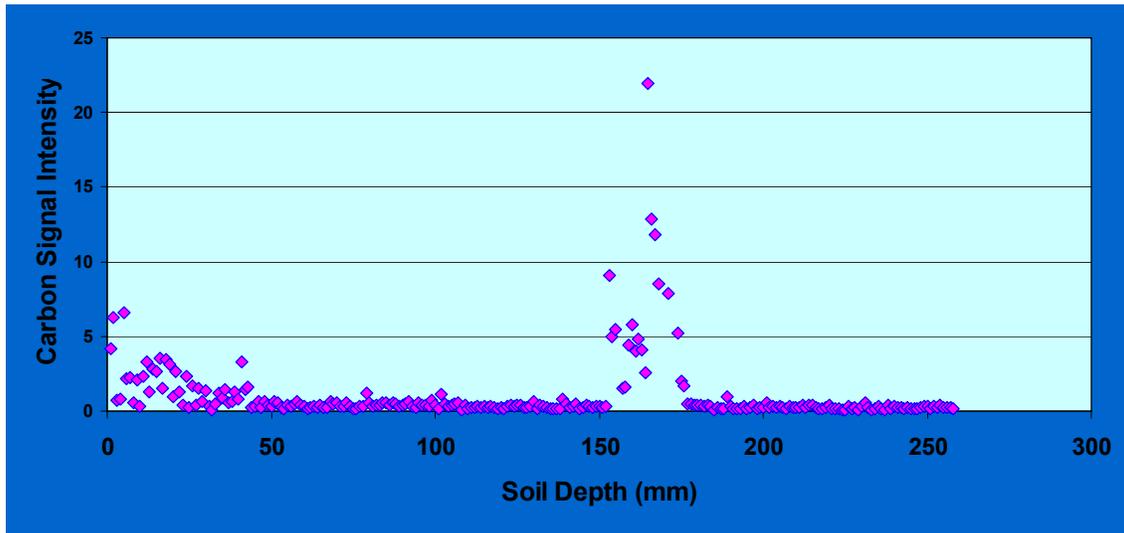


Fig. 4 Phosphorus Calibration Curve (Spiked Soil)

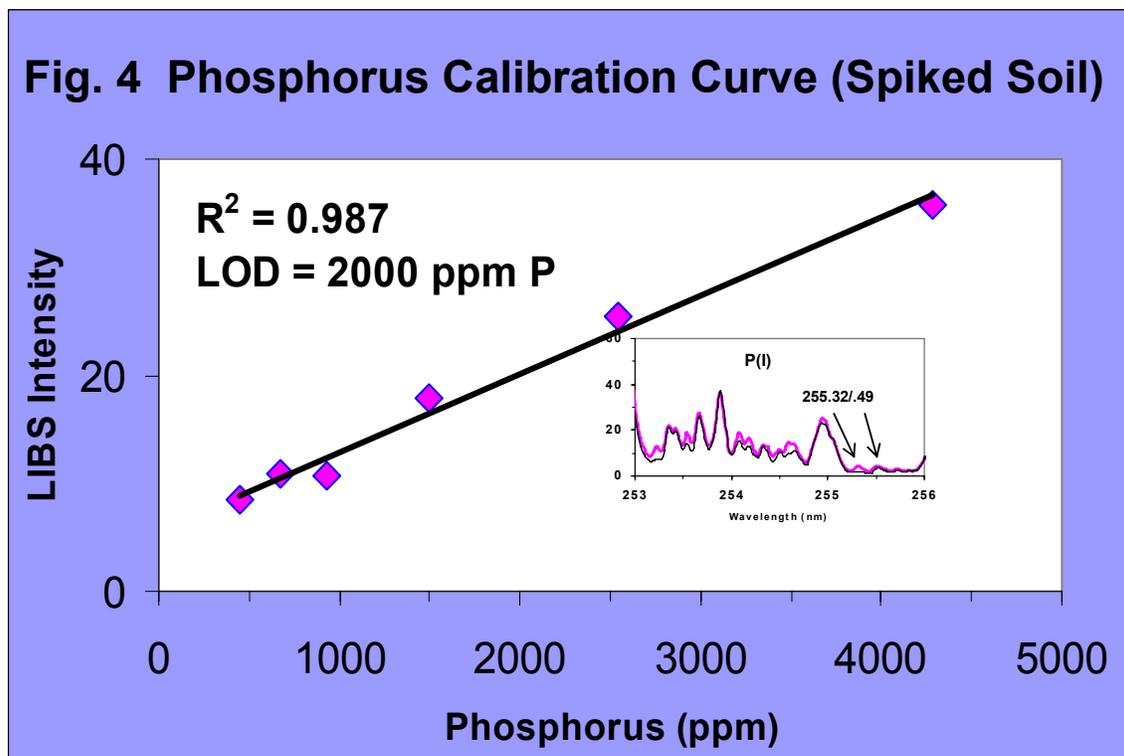


Fig. 5 Nitrogen Calibration Curve (Sand/Clay)

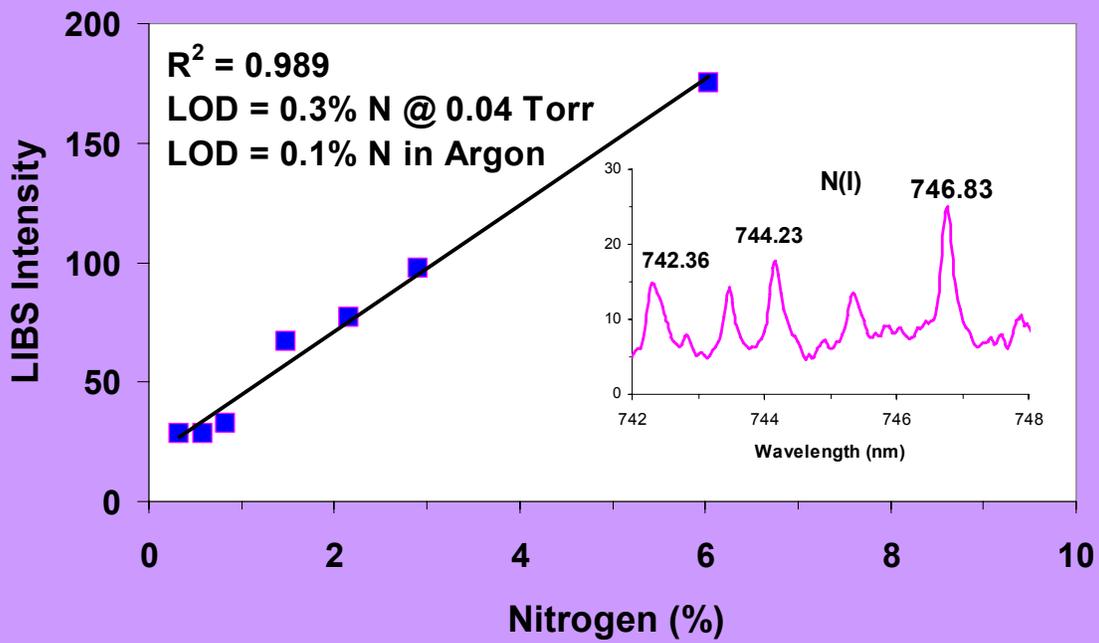


Fig. 6 Sulfur Calibration Curve (Sand/Clay)

