

Measuring Total Soil Carbon with Laser-Induced Breakdown Spectroscopy

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Terrestrial carbon fluxes account for more than half of the carbon transferred between the atmosphere and the Earth's surface (about 120 gigatons/yr), and current stores of carbon in terrestrial ecosystems are estimated at 2,060 gigatons. Given humanity's ability to modify terrestrial systems and, hence, to control these fluxes, management and sequestration of carbon in the terrestrial biosphere has emerged as the most promising near-term means of mitigating overall U.S. carbon emissions, as highlighted in the 1999 Department of Energy Carbon Sequestration Report. We are in the process of testing a new spectroscopic method for measuring total soil carbon, based on laser-induced breakdown spectroscopy (LIBS).

Much of the carbon in terrestrial ecosystems is in the form of soil carbon, which is the fundamental building block of soil organic matter. Consequently, soil carbon is a primary determinant of many soil chemical and physical properties, including nutrient availability, soil structure, and water-holding capacity, all of which directly influence ecosystem productivity and land quality.

Soil carbon measurement is the focus of current and future international negotiations and treaties related to global climate change. To manage terrestrial carbon inventories and fluxes effectively, it is important to find more efficient ways to measure soil carbon. It is possible that we may need orders of magnitude more measurements than have been obtained to date.

The LIBS method is based on atomic-emission spectroscopy. In this method, a laser is focused on a solid sample and forms a microplasma that emits light characteristic of the elemental composition of the sample. The emitted light is collected, spectrally resolved, and detected to monitor concentrations of elements via their unique spectral signatures. When calibrated, the LIBS method provides quantitative measurements. This method is readily amenable for field-portable instrumentation and high-throughput analysis.

In the discussion below of our preliminary work, we evaluate the LIBS method to measure total soil carbon and test the hypothesis that the LIBS carbon signal is correlated with total soil carbon. Our results suggest that the LIBS method provides a useful new approach for measuring total soil carbon.

Methods

To assess ways to detect carbon using existing LIBS technology, we evaluated different carbon emission lines that are produced by LIBS and selected a strong emission peak occurring at 247.8 nm to use for measuring carbon. A laser (type Nd:YAG) set at a wavelength of 1,064 nm (50-mJ pulses of 10 ns) was focused with a lens of 50-mm focal length on each soil sample (Figure 1). The light was collected by a fused silica fiber-optic cable pointed at the plasma from a distance of about 50 mm. A spectrograph of 0.5-m focal length resolved the light that was then detected using a gated-intensified photodiode array detector.

For each LIBS analysis, a sample was placed in a 25- μm -diameter \times 75- μm -long quartz tube, which was then positioned such that the focal volume of the laser pulse was centered in the tube. Twenty laser pulses were directed into the tube to

complete one measurement. Typical measurement areas for the LIBS method are 1 to 5 mm²/pulse. The background signals from carbon and silicon emissions were subtracted from the resulting spectrum, and this procedure was repeated for each sample. Because of shot-to-shot variations in the laser plasma parameters and sampling geometry, measurement precision is increased by taking the ratio of the analyte signal to the signal from another species, in this case silicon, with the same concentration assumed in all samples.

We measured total soil carbon with the conventional dry combustion method using a Dohrmann DC-180 analyzer and then with LIBS to calibrate, verify, and assess performance of our LIBS method. We calibrated and tested the LIBS measurements using soils from a series of farms in east-central Colorado and soils from a piñon-juniper woodland near Los Alamos, New Mexico.

The total soil carbon concentrations from a subset of the Colorado samples were measured using dry combustion, and these soil concentrations were used to verify the calibrated LIBS method against (1) different samples from a subset of the same soils and (2) soils of distinctly different parent material and genesis (alfisols weathered from

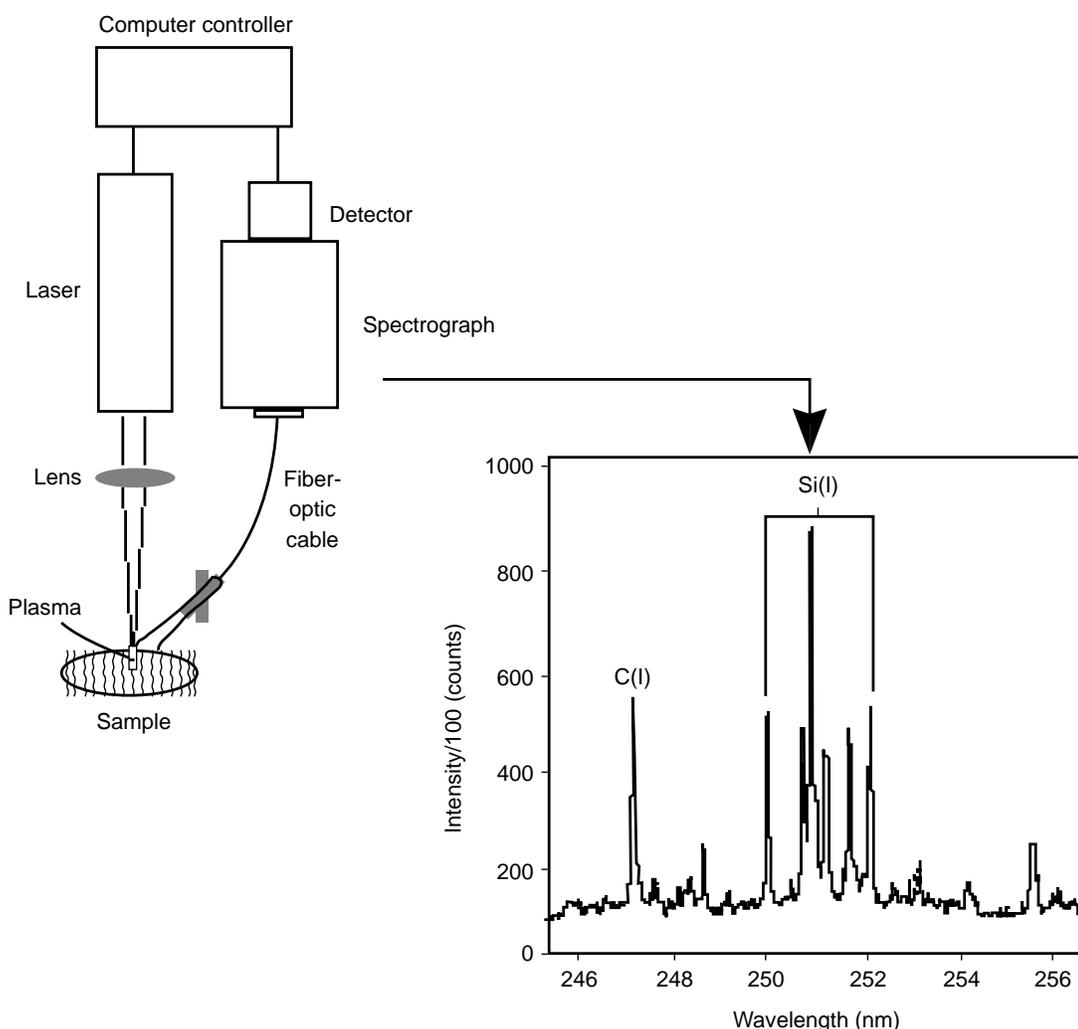


Figure 1. The LIBS Apparatus.

This diagram of the apparatus shows a LIBS spectrum of a soil tuned to monitor the carbon emission at 247.8 nm. To the right of the carbon line is a series of silicon lines used for quantification.

volcanic tuff in the piñon-juniper woodland near Los Alamos).

The Colorado soil samples were collected from cultivated plots in mollisols weathered from sandstone that were conventionally tilled. Samples were collected from random locations in the fields after harvest from 0 to 10 cm and 10 to 20 cm below the soil surface. The piñon-juniper woodland samples were collected under piñon trees (*Pinus edulis*) or juniper trees (*Juniperus monosperma*) or in intercanopy spaces that were either grass-covered or bare. These piñon-juniper samples were collected in 5-cm intervals to 30 cm or until parent material was observed. Each sample was sieved to

<2 mm, air dried, then analyzed by dry combustion and LIBS.

We evaluated LIBS measurement performance from the collected data. A detection limit (DL) for carbon was estimated using the formula $DL = 3\sigma/m$, where σ is the standard deviation of 6 to 12 replicate measurements and m is the slope of the calibration curve. We estimated the measurement precision by performing 6 to 12 replicate measurements on several samples and computing the percent relative standard deviation. Accuracy was estimated by comparing LIBS measurements to dry combustion measurements obtained from two different laboratories.

Results

We determined that carbon could be identified and quantified using LIBS. A plot of the LIBS signal versus carbon concentration for soils from the cultivated plots (Colorado samples) shows excellent correlation and provides a calibration curve (Figure 2a). The calibration curve was effective in predicting the carbon content of additional samples from the cultivated plots (Figure 2b). The same calibration curve was also effective in predicting carbon concentrations in semiarid alfisols (Los Alamos samples), even though the genesis of the soils was

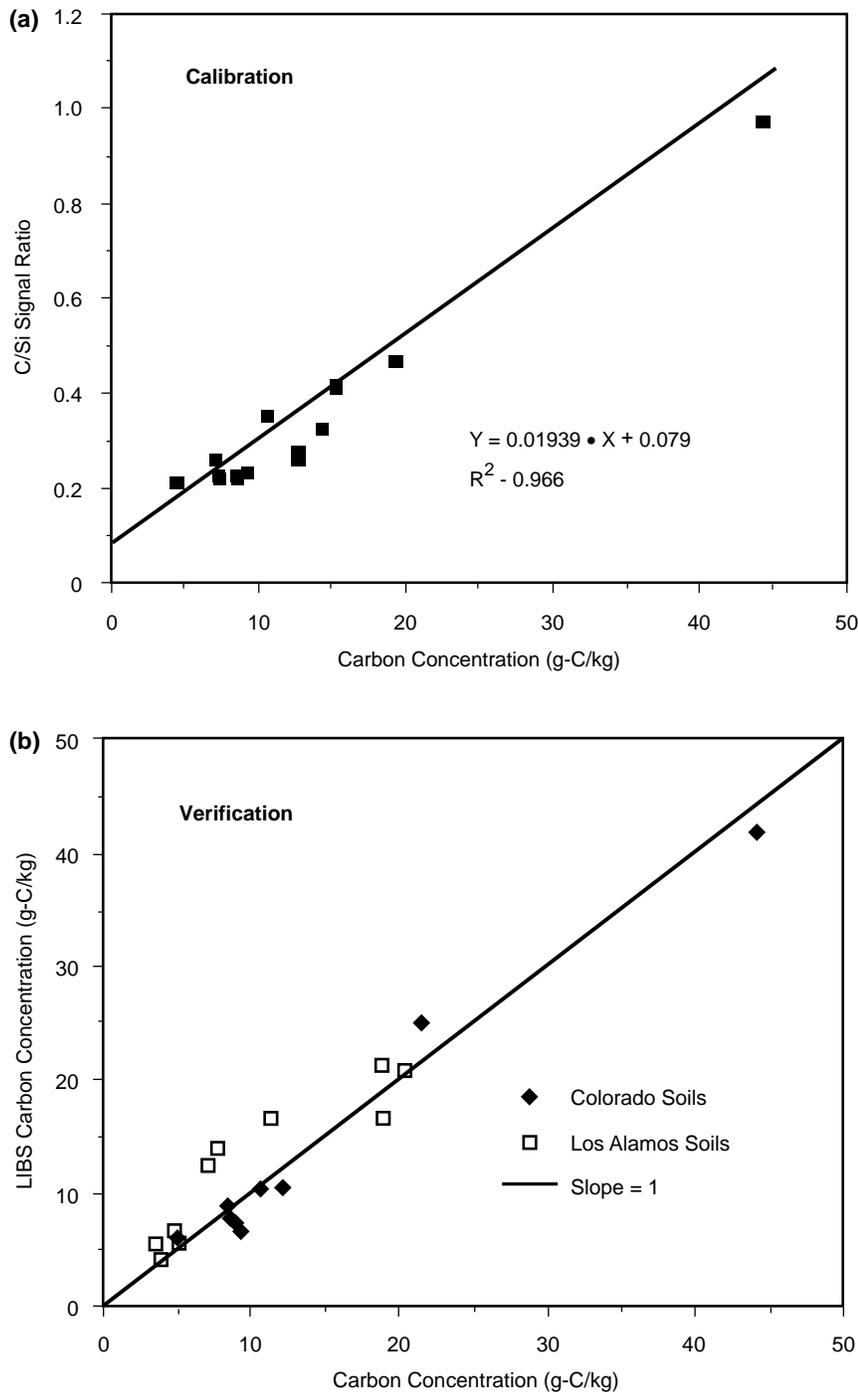


Figure 2. LIBS Soil Data.

(a) Calibration curve for the detection of total soil carbon from Colorado mollisols. The data show a strong relationship between the LIBS signal and total soil carbon.

(b) Correlation between the predicted carbon concentration by LIBS and the percent carbon determined by dry combustion for Colorado mollisols and Los Alamos alfisols. The line indicates exact correlation between LIBS measurements and dry-combustion determinations.

significantly different (Figure 2b). The effectiveness of the calibration curve supports our hypothesis that the magnitude of the carbon signal detected by LIBS is a good indicator of the total soil carbon concentration. We estimated LIBS detection limit to be 300 mg-C/kg⁻¹ with precision of 4 to 5% and accuracy of 3 to 14%.

Conclusion

Our initial work on application of the LIBS method to total soil carbon measurement suggests that LIBS can provide rapid and efficient measurements of total soil carbon with appropriate limits of detection, accuracy, and precision. Good carbon measurements with LIBS were obtained with two distinct soil types. Additional work is needed to evaluate if measurements must be adjusted for effects such as soil type and texture, a wide range in carbon concentration, carbonate, bulk density, and soil water content. In addition, we are evaluating the feasibility of incorporating a constant silicon standard in the method to avoid variation in soil silicon due to changes in mineralogy among soil samples. Because LIBS can be made field portable and has short sample analysis time, it could be very useful for obtaining large numbers of carbon measurements in the field. Our preliminary findings suggest that the LIBS method may help to address carbon measurement and management issues in range land, agricultural, and forest ecosystems. ■

Collaborator

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Further Reading

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