
SHORT COMMUNICATIONS

Measuring Total Soil Carbon with Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract

Improving estimates of carbon inventories in soils is currently hindered by lack of a rapid analysis method for total soil carbon. A rapid, accurate, and precise method that could be used in the field would be a significant benefit to researchers investigating carbon cycling in soils and dynamics of soil carbon in global change processes. We tested a new analysis method for predicting total soil carbon using laser-induced breakdown spectroscopy (LIBS). We determined appropriate spectral signatures and calibrated the method using measurements from dry combustion of a Mollisol from a cultivated plot. From this calibration curve we predicted carbon concentrations in additional samples from the same soil and from an Alfisol collected in a semiarid woodland and compared these predictions with additional dry combustion measurements. Our initial tests suggest that the LIBS method rapidly and efficiently measures soil carbon with excellent detection limits (~300 mg/kg), precision (4–5%), and accuracy (3–14%). Initial testing shows that LIBS measurements and dry combustion analyses are highly correlated (adjusted $r^2 = 0.96$) for soils of distinct morphology, and that a sample can be analyzed by LIBS in less than one minute. The LIBS method is readily adaptable to a field-portable instrument, and this attribute—in combination with rapid and accurate sample analysis—suggests that this new method offers promise for improving measurement of total soil carbon. Additional testing of LIBS is required to understand the effects of soil properties such as texture, moisture content, and mineralogical composition (i.e., silicon content) on LIBS measurements.

SOIL carbon is the fundamental building block of soil organic matter and as such it is a primary determinant of many soil chemical and physical properties including nutrient availability, soil structure, and water-holding capacity (Lal, 1997, 1999), all of which directly influence soil quality and ecosystem productivity. Soil carbon measurement is the focus of current and future international negotiations and treaties related to global change. However, more efficient methods of measuring soil carbon are required to support better estimates of terrestrial carbon inventories and fluxes for their effective management (National Research Council, 1999). Improved terrestrial carbon inventories may require or-

ders of magnitude more measurements than can be delivered economically using current technology.

Developing more efficient methods of measuring soil carbon is a pressing need to address global climate change and terrestrial carbon management issues (Greenland, 1998; Department of Energy, 1999; McCarty and Reeves, 2001). Over the past two decades, several advanced analytical methods have been applied to the study of soil carbon. Estimating the retention time and rates of turnover of carbon in soils (e.g., Paul et al., 2001), the formation rates of components of soil organic carbon (e.g., Horwath et al., 2001), and the source or history of carbon that comprises soil organic carbon (e.g., Scharpenseel et al., 2001) have been addressed via carbon isotope techniques. The composition of soil organic matter has also been evaluated by new applications of instrumental laboratory analyses (e.g., McCarty and Reeves, 2001; Rossell et al., 2001), and total soil carbon has been quantified using infrared spectroscopy (e.g., Ben-Dor and Banin, 1995; Ludwig and Khanna, 2001).

Here we report preliminary results of a new spectroscopic method for measuring total soil carbon that is based on laser-induced breakdown spectroscopy (LIBS). The LIBS method is based on atomic emission spectroscopy (Radziemski and Cremers, 1989; Moenke-Blankenburg, 1989; Rusak et al., 1997). 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 method provides quantitative measurements. The method is readily amenable for field-portable instrumentation (Cremers et al., 1996; Yamamoto et al., 1996) and high-throughput analysis. We evaluated the LIBS method for its potential to measure total soil carbon, and specifically tested the hypothesis that the LIBS carbon signal is correlated with total soil carbon, which could thereby provide a useful new approach for measuring total soil carbon.

Methods

We selected the strong carbon C(I) emission line at 247.8 nm for this test and calibration of LIBS (Alkemade et al., 1978; Boutillier et al., 1978). A Nd:YAG laser (Spectra-Physics Lasers, Mountain View, CA) at a wavelength of 1064 nm (50-mJ pulses of 10 ns) was focused with a lens of 50 mm focal

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Abbreviations: LIBS, laser-induced breakdown spectroscopy.

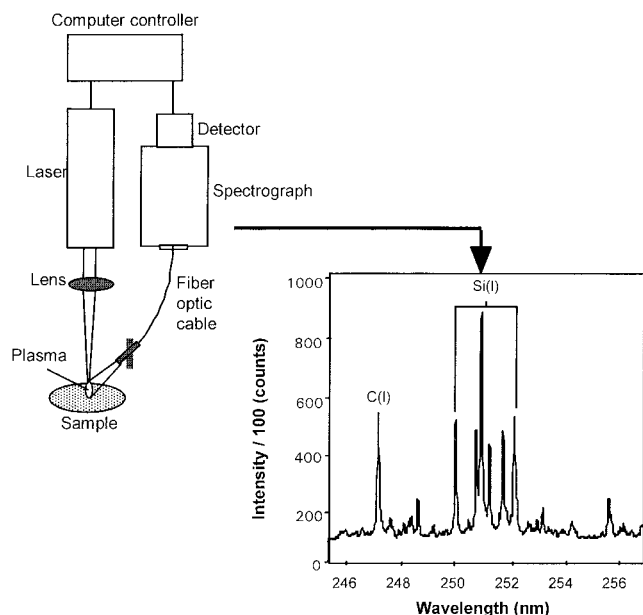


Fig. 1. Diagram of laser-induced breakdown spectroscopy (LIBS) apparatus showing a LIBS spectrum of a soil tuned to monitor the carbon emission at 247.8 nm. To the right of the carbon line is a series of silicon lines used for quantification.

length on each soil sample (Fig. 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 quartz tube of 25 mm diameter by 75 mm long, 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 mm³/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 ratioing 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 (Tekmar-Dohrmann, Mason, OH) (Nelson and Sommers, 1982; Sollins et al., 1999; Robertson and Paul, 2000) and with LIBS to calibrate, verify, and assess performance of our LIBS method. We calibrated and tested the LIBS measurements using two Aridic Argiustolls, an Aridic Paleustoll, and an Ustic Torriorthent, all of which were weathered from sandstone and collected from conventionally tilled farms in east-central Colorado (Crabb, 1982; Petersen et al., 1986; Catlett, 2000), and a Typic Haplustalf from a piñon (*Pinus edulis* Engelm.)–juniper [*Juniperus monosperma* (Engelm.) Sarg.] woodland near Los Alamos, New Mexico (Davenport et al., 1996; Newman, 1996; Reid, 1997). The total soil carbon concentration from a subset of the Colorado samples was measured by dry combustion and then used to verify the calibrated LIBS method against different samples from the same soils; in addition, soils from Los Alamos were included in the verification because they were of distinctly different parent material (volcanic tuff) and genesis. The Colorado 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 or juniper trees, or in intercanopy spaces that were either grass-covered or bare. The piñon–juniper soils were collected in 5-cm intervals to 30 cm or until parent material was observed. Each sample was air-dried, sieved to <2 mm (not ground), 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 (% RSD). 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 (Fig. 2A). The calibration curve was effective in predicting the carbon content of additional samples from the cultivated plots (Fig. 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 significantly different (Fig. 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 the LIBS detection limit to be 300 mg C/kg with precision of 4% to 5% and accuracy of 3 to 14%.

Discussion

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. Measurements of total soil carbon by dry combustion are highly correlated with LIBS measurements of the same samples, and thus indicate that LIBS analyses provide similar information about soil carbon concentrations (Fig. 2A). Analysis of additional samples from two different locations by LIBS and dry combustion confirmed that the two methods provide nearly identical results, at least with the selected soils (Fig. 2B). The initial results also provide guidance for additional research that is needed in order to apply LIBS data to questions about carbon dynamics in soils. In general, the LIBS method should be tested and verified on a more comprehensive suite of soils to determine if the high correlations we found for two soils apply to additional soils, or, in case the correlations do not hold, what adjustments in the method are needed. More specifically, the effects of various soil properties on the LIBS measurements and associated estimates of total soil carbon need to be accounted for as part of future research and to determine the broader applicability of LIBS analyses. Soil properties that could influence LIBS

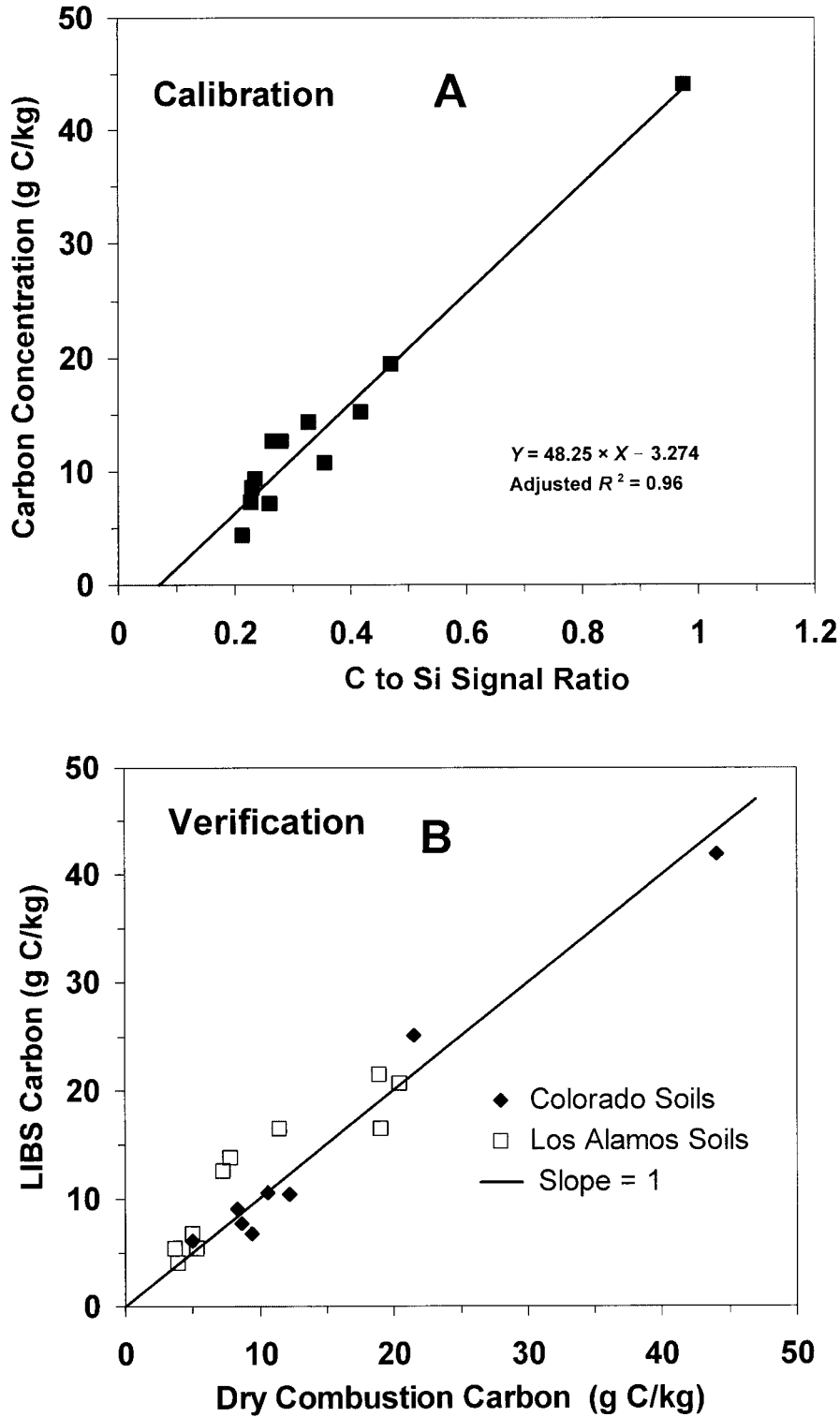


Fig. 2. (A) Calibration curve for the detection of total soil carbon from Colorado Mollisols using laser-induced breakdown spectroscopy (LIBS). (B) Correlation between carbon concentration predicted by LIBS and determined by dry combustion for Colorado Mollisols and Los Alamos Alfisols. Line indicates exact correlation between LIBS and dry combustion measurements.

analyses include soil texture, the range of total soil carbon that can be reliably detected, the effects of carbonates on LIBS measurements (and possible treatments to remove carbonate-carbon without altering organic carbon), and the effects of soil moisture. In addition, the use of ratios of the carbon signal to the silicon signal

from LIBS spectra should be evaluated with regard to soil mineralogy since the silicon content of soils varies with the mineralogy of the soil. Understanding the effects of soil properties and clay mineralogy on the LIBS measurements will provide the information needed to establish the range of effectiveness for LIBS analyses.

The LIBS method promises to be a rapid method of analyzing total soil carbon. Samples can be analyzed with the present laboratory-based instrument in less than one minute, and the potential daily throughput is currently in excess of two hundred samples. With this capability, the limitations to analysis of carbon in soils at spatially meaningful scales (e.g., from plot scale to patch scale or larger) are the accessibility of the sites and statistical adequacy of sampling designs, not the time needed for analysis of samples. This capability is required as a more detailed and mechanistic understanding of the carbon cycle in soils is needed to evaluate issues such as global change and in setting environmental policies regarding greenhouse gases.

Measuring total soil carbon in situ is essential for accurately estimating carbon inventories in different landscapes and ecosystems. The potential of using LIBS in the field and on soil profiles in situ is a unique potential application of the method. We are currently developing a field-portable LIBS instrument with precision and accuracy comparable with the laboratory-based instrument presented here. Such an instrument could be used to analyze samples in a variety of locations, and could also be capable of analyzing soil carbon at depth from intact profiles.

In conclusion, addressing spatial variability of carbon concentrations in soils is a key step to a better understanding of carbon cycling in terrestrial ecosystems. The speed of the new LIBS analysis method and the ease of collecting data either in situ or from soil cores in the field provide an efficient means to analyze the number of samples needed to estimate inventories of carbon in soils of various ecosystems. A more complete understanding of the terrestrial carbon cycle is a critical part of a sustainable carbon management strategy designed to enhance soil carbon where it has been depleted, store increased amounts of carbon in soils where feasible, and simultaneously minimize net carbon loss from rangeland, agricultural systems, and forest ecosystems.

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Rapid, Sensitive, Microscale Determination of Phosphate in Water and Soil

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Abstract

A rapid and sensitive analysis of inorganic and organic phosphorus (P) is needed to analyze water and soil extracts at submicromolar concentrations. The proposed method, based on the complexation of malachite green with phosphomolybdate under acidic conditions, was adapted to a 96-well microtiter plate format, and was tested for matrix interferences using 15 soils and some common extractants, including water, KCl, CaCl_2 , NaOH, and HCl. The accuracy of P determination was affected when CaCl_2 and HCl concentrations were greater than 0.1 M and when NaOH concentration exceeded 0.4 M. Potassium chloride concentration up to 1 M did not interfere with P determination. The molar absorptivity was $46\,841\ \text{M}^{-1}\ \text{cm}^{-1}$ and the reagent blank absorbance was 0.071 ± 0.003 ($n = 10$). At the 99% confidence limit, the method detection limit was calculated to be $0.006\ \text{mg P L}^{-1}$. Recovery of added inorganic P in different types of soils and extracts ranged between 95 and 112% with an average of 102%. The proposed microplate method allows P to be determined rapidly in a wide range of soil types and extracts and requires limited volume (20–200 μL). The procedure uses limited quantities (40 μL) of two stable reagents (>1 yr), and generates low amounts of hazardous waste.

PHOSPHORUS is a key nutrient needed for the growth of plants and animals and is a common nonpoint-source pollutant contributing to eutrophication of surface water bodies. Hence, routine analysis of P in surface water samples and soils constitutes a major workload in agricultural and environmental chemistry laboratories. For example, between 1995 and 1997, more than 7500 surface and ground water samples were analyzed by the Kentucky Division of Water to comply with Section 305(b) of the Clean Water Act, which mandates states to continually monitor for P and other environmental contaminants.

Current approved methods for determination of soluble inorganic P ($\text{PO}_4^{3-} + \text{HPO}_4^{2-} + \text{H}_2\text{PO}_4^- + \text{H}_3\text{PO}_4$) in water include manual and automated colorimetric techniques and ion chromatography (American Public Health Association, 1998). Both methods have their strengths and weaknesses. Ion chromatography, for ex-

ample, is not widely used because it has a relatively high detection limit ($0.1\ \text{mg L}^{-1}$) and cannot be used for samples with high concentrations of interfering anions without sample pretreatment. The automated ascorbic acid colorimetric method is extensively used because it overcomes most of these obstacles. Moreover, many automated techniques can save time when they are configured to simultaneously determine several components in a sample mixture. However, many automated techniques require expensive and dedicated equipment and a high degree of technical expertise to operate, and generate large volumes of waste. Considering the short holding time for analysis of soluble inorganic P (<48 h for refrigerated samples) and the number of samples involved, these constraints put a burden on many laboratories.

The malachite green (MG) colorimetric procedure has also been used to determine P at submicromolar concentrations in water and soil-water extracts (van Veldhoven and Mannaerts, 1987; Ohno and Zibilske, 1991). Both the ascorbic acid (AA; Murphy and Riley, 1962) and MG methods rely on complex formation with phosphomolybdate under acidic conditions. However, Ohno and Zibilske (1991) found that the MG method was about 3.3 times more sensitive than the AA method. An additional strength of the MG method is reagent stability (>1 yr) (van Veldhoven and Mannaerts, 1987).

Our laboratory routinely analyzes inorganic P and total P in a wide range of samples, including water samples collected from lakes and wetlands, and agricultural soils amended with inorganic fertilizer and manure. Phosphorus concentrations in oligotrophic systems can be $<0.01\ \text{mg P L}^{-1}$, which are difficult to analyze routinely with AA and ion chromatography. We commonly extract soil samples using different chemicals to determine the forms of P in different fractions, which also presents analytical problems with respect to P determination. Thus, we were interested in developing a single rapid, precise, sensitive, and accurate method to determine P in samples generated from such studies.

Large numbers of analytical determinations can be accomplished by conducting established colorimetric reactions in disposable plastic or glass 96-well microplates (typically in an 8 by 12 configuration with each well having a volume of about 0.5 mL) and measuring absorbance of the wells using a microplate reader. Essen-

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