Total Carbon Measurement in Soils using Laser-Induced Breakdown Spectroscopy: Results from the Field and Implications for Carbon Sequestration

Michael H. Ebinger
(mhe@lanl.gov, 505-667-3147)
Environmental Dynamics and Spatial Analysis Group (EES-10), MS J495
Earth and Environmental Sciences Division
Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

David A. Cremers
(cremers_david@lanl.gov, 505-665-4180)
Advanced Chemical Diagnostics and Instrumentation Group, MS J565
Chemistry Division
Los Alamos National Laboratory, Los Alamos, NM 87545

David D. Breshears
(daveb@lanl.gov, 505-665-2803)
Environmental Dynamics and Spatial Analysis Group (EES-10), MS J495
Earth and Environmental Sciences Division
Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

Pat J. Unkefer
(punkefer@lanl.gov, 505-665-2554)
Bioscience Division, B-S1, MS E529
Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

Susan A. Kammerdiener
Environmental Dynamics and Spatial Analysis Group (EES-10), MS J495
Earth and Environmental Sciences Division
Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

Monty J. Ferris
Advanced Chemical Diagnostics and Instrumentation Group, MS J565
Chemistry Division
Los Alamos National Laboratory, Los Alamos, NM 87545

LA-UR-01-1097

ABSTRACT

Rapid measurement of total carbon in soils is an important factor in modeling the effects of global change and carbon sequestration in soils. Conventional methods of carbon analysis such as dry combustion are relatively slow, and reliable estimation of carbon concentrations at the landscape scale is practically impossible because of the need for many replicate measurements. A new spectroscopic method, laser-induced breakdown spectroscopy (LIBS), provides rapid carbon analysis with little or no sample preparation time. LIBS is portable and can be used for carbon analysis in the field or even *in situ*, such as inside a soil borehole. Data from LIBS analyses can be used to monitor small changes in soil carbon at different times, a critical component in many global climate models and terrestrial carbon sequestration strategies. We present a comparison of dry combustion measurements with LIBS analyses using several agricultural and woodland soils. The LIBS data are highly reproducible, are not affected by differences in soil types, and there is a strong correlation with dry combustion measurements. We further show the results of carbon measurements in different parts of a piñon-juniper woodland in semiarid New Mexico. Our results highlight soil carbon concentrations under tree canopies, in intercanopy spaces, and in small-scale catchments within the woodland. The latter measurements show an important, but until use of LIBS, overlooked store of carbon in semiarid areas. The use of LIBS data shows many benefits including reducing the uncertainty inherent in measurements of soil carbon in different environments, the speed with which LIBS analyses can be obtained (minutes) compared to dry combustion (days), and in modeling the global cycling of carbon in terrestrial settings. LIBS analyses make possible the estimation of landscape-scale carbon inventories that require large sample numbers as well as detailed quantification of carbon concentrations in soils under canopies or unvegetated patches.

INTRODUCTION AND OBJECTIVES

Rapid and accurate measurement of carbon in soil samples is essential to evaluate the amount of carbon that can be sequestered in soils and for modeling global change. Uncertainty in current estimates of terrestrial carbon inventories not only add to the uncertainty of predicted effects of global change, but also make difficult a thorough understanding of the processes and dynamics of the carbon cycle. Conventional analytical methods for total soil carbon involve removing samples from test areas and conducting analysis in an analytical laboratory; both steps require significant resources of time and manpower to complete. In addition, analysis of large numbers of soil samples in order to reduce uncertainty in carbon inventory measurements requires significant disturbance of soil-plant systems. The resulting environmental impact could be deleterious to the ecosystem under study.

Laser-induced breakdown spectroscopy (LIBS) is a new method for analysis of total soil carbon that is rapid, can be done in the field with minimal soil disturbance and eventually *in situ*, and offers unprecedented capability for analysis of large numbers of samples. We calibrated LIBS for analysis of total carbon from soils with samples from agricultural fields and from a long-term ecological test area and show the results of the calibration below.

The main goal of this work was to evaluate the capabilities of LIBS as a rapid, accurate, and potentially field-portable method of total carbon analysis for soils. Our objectives were:

- calibrate LIBS against conventional methods of carbon analysis (dry combustion) to measure concentrations of total soil carbon;

- verify the calibration with different samples from the same fields as the calibration samples;
- evaluate the calibration and predictive capability with soil samples from distinct geographic areas and soils of different genesis.

APPROACH

Laser-induced breakdown spectroscopy is an analytical technique that has the potential to change drastically the way total carbon is measured in soils. The LIBS method involves focusing a laser on a soil sample and collecting the light emitted from the sample as a result of the laser excitation. The emitted light is characteristic of the elemental composition of the sample, thus the amount of carbon in the sample can be quantified (Alkemade et al., 1978; Boutilier et al., 1978; Cremers et al., 1996)

A Nd:YAG laser at a wavelength of 1064 nm (50 mJ pulses of 10 ns) was focused on each soil sample, and the emitted light was collected by a fiber optic cable. A 0.5 m spectrograph resolved the light that was then detected using a photodiode array detector. For each analysis a sample was placed in a quartz tube of 25 mm diameter by 75 mm long, and twenty laser pulses were directed into the tube to complete one measurement. Typical measurement areas for the LIBS method are 1 to 5 mm^3/pulse. The background signals from carbon and silicon were subtracted from the resulting spectrum.

We measured total soil carbon by conventional dry combustion using a Dohrmann DC-180 analyzer (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 with soils from farms in east-central Colorado (Crabb, 1982; Petersen et al., 1986; Catlett, 2000) and soils from a piñon-juniper woodland near Los Alamos, New Mexico (Davenport et al., 1996; Newman, 1996; Reid, 1997). Total soil carbon was measured from a subset of the Colorado samples by dry combustion and then by LIBS to test if the calibrated LIBS predicted carbon from (1) different samples collected from the same fields as the calibration samples, and (2) soils of distinctly different genesis. Calibration and verification samples were collected from random locations in the Colorado fields after harvest from 0 to 10 cm and 10 to 20 cm below the soil surface. Samples from the piñon-juniper woodland were collected under 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 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 to12 replicate measurements and m is the slope of the calibration curve. The measurement precision was estimated by performing 6 to 12 replicate measurements on several samples and computing the %RSD (percent relative standard deviation). Accuracy was estimated by comparing LIBS measurements to dry combustion measurements obtained from two different laboratories.

RESULTS

LIBS calibration using the Colorado soils was excellent in comparison to total carbon data obtained from convention al methods (Figure 1). The calibration allows translation of the raw LIBS signal to total carbon concentration in soil samples with a high degree of certainty. We tested the calibration using new soil samples from the same fields from which the calibration samples were collected, and the carbon concentration predicted with LIBS was again in excellent agreement with dry combustion data (Figure 2). The results of the second test of the LIBS method was conducted with the piñon-juniper soils, and again the LIBS data predicted carbon concentrations similar to those obtained with dry combustion analysis (Figure 2). The Los Alamos soils are of a different soil genesis than the Colorado soils and are the first test of LIBS obtained from distinct soil types. Finally, the LIBS detection limit was estimated at about 300 mg-C kg^{-1} with precision of 4% to 5% and accuracy of 3 to 14%. For comparison, the detection limit of dry combustion was about 1000 mg-C kg^{-1}, precision was 2% to 10%, and precision was 3% to 12%.

CONCLUSIONS

We showed that the LIBS method could be calibrated to analyze for total carbon in soils, and the agreement between the dry combustion method and LIBS analysis was excellent. The degree of correlation between the methods indicates that LIBS is indeed a powerful tool for total carbon analysis in soils. We also showed that the calibration curve could predict the carbon concentration in soils that were collected from the same fields from which the calibration samples were collected. We expected that the LIBS method would perform well in this particular test because the soils were of similar genesis as the calibration soils. Further, the LIBS method had to prove accurate and precise when analyzing samples of similar genesis in order for the method to be widely applicable to carbon sequestration work. In addition, the LIBS method proved accurate in predicting the carbon concentration from soils that were of distinct genesis, an attribute of LIBS that further supports the applicability of the method. Overall, LIBS is an exciting new method of analysis for total soil carbon that appears to be unaffected by differences in soil formation properties. We are currently testing LIBS over a broad range of soil types in order to evaluate the sensitivity of carbon measurements to various soil properties such as texture, mineralogy, and drainage classification.

The main advantages to using LIBS are 1) to provide accurate yet rapid measurements of total soil carbon; 2) to provide these data in a cost-effective manner, 3) to show the capabilities of measuring total soil carbon in the field; and 4) to estimate the spatial variability in total soil carbon by analysis of a large number of samples from study areas. Carbon data from LIBS measurements will 1) enable detailed analysis of large study areas for the distribution of carbon in soils; 2) allow for intensive characterization of small study areas to isolate those parameters important to carbon cycling; 3) result in minimal soil disturbance even though a large number of samples from a given area can be analyzed; and 4) foster the field analysis of large numbers of samples in a short time frame. These features of LIBS analysis will help revolutionize the measurement of carbon in soils and greatly improve estimates of carbon in soils and ecosystems.

References Cited

Alkemade, C.Th.J., W. Snelleman, G. D. Boutilier, B. D. Pollard, J. D. Winefordner, T. L. Chester, and N. Omenetto. 1978. Review and tutorial discussion of noise and signal-to-noise ratios in analytical spectrometry, 1. Fundamental principles of signal-to-noise ratios. Spectrochimica Acta, 33B 383-399.

Boutilier, G.D., B. D. Polard, J. D. Winefordner, T. L. Chester, and N. Omenetto. 1978. Review and tutorial discussion of noise and signal-to-noise ratios in analytical spectrometry, 2. Fundamental principles of signal-to-noise ratios. Spectrochimica Acta: 33B 401-416.

Catlett, K.M. 2000. The role of organic matter and other soil properties in Zn^{2+} activity and AB-DTPA-extractable Zn in Soils. Ph . D. dissertation, Department of Soil and Crop Sciences, Colorado State University, Ft. Collins.

Crabb, J.A. 1982. Soil Survey of Weld County, Colorado, North Part. USDA, Soil Conservation Service, Washington.

Cremers, D.A., M. J. Ferris, and M. Davies. 1996. Transportable laser-induced breakdown spectroscopy (LIBS) instrument for field-based soil analysis. Proceedings of the Society of Photo-Optical Instrumentation Engineers, 2835 190-200.

Davenport, D.W., B. P. Wilcox, and D. D. Breshears. 1996. Soil morphology of canopy and intercanopy sites in a piñon-juniper woodland. Soil Science Society of America Journal, 60 1881-1887.

Nelson, D.W. and L. E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-579*In* Page, A. L., R. H. Miller, and D. R. Keeney (eds) Methods of Soil Analysis, Part 2--Chemical and Microbiological Properties, Second edition. American Society of Agronomy / Soil Science Society of America, Madison.

Newman, B.D. 1996. Geochemical investigations of calcite fracture fills and mesa-top water dynamics on the Pajarito Plateau, New Mexico. Ph . D. dissertation, New Mexico Institute of Mining and Technology, Socorro and Los Alamos National Laboratory Report LA-UR-96-1441, Los Alamos, N.M.

Petersen, M.L., J. A. Crabb, and R. J. Larsen. 1986. Soil Survey of Washington County, Colorado. USDA Soil Conservation Service, Washington.

Reid, K.D. 1997. Runoff and sediment yield in a semiarid piñon-juniper woodland, New Mexico. M. S. thesis, Department of Earth Resources, Colorado State University, Ft. Collins.

Robertson, G. P. and E. A. Paul. 2000. Decomposition and soil organic matter dynamics. p. 104-116 *In* Sala O. E., R. B. Jackson, H. A. Mooney, and R. W. Howarth (eds.) Methods in Ecosystem Science, Springer, New York.

Sollins, P., C. Glassman, E. A. Paul, C. Swanston, K. Lajtha, J. W. Heil, and E. T. Elliott. 1999. Soil carbon and nitrogen: pools and fractions. p. 89-105 *In* Sala O. E., R. B. Jackson, H. A. Mooney, and R. W. Howarth (eds.) Methods in Ecosystem Science, Springer, New York.

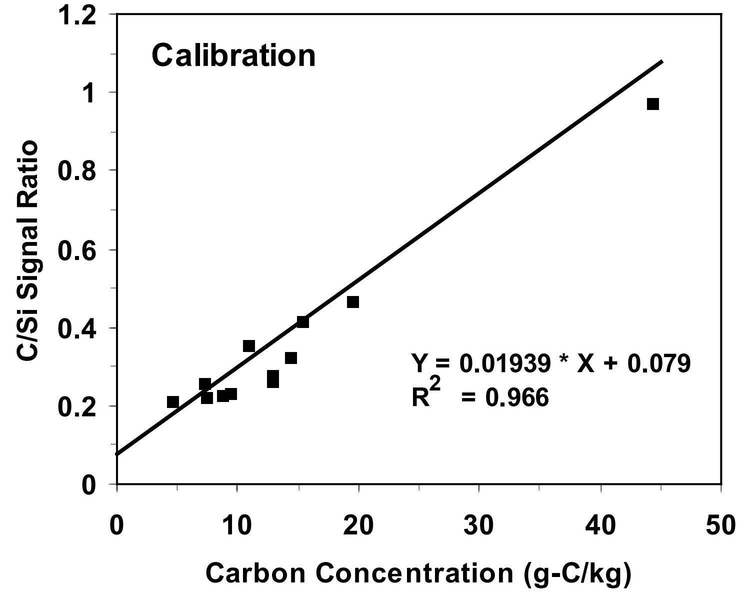

Figure 1. LIBS calibration curve with Colorado soils.

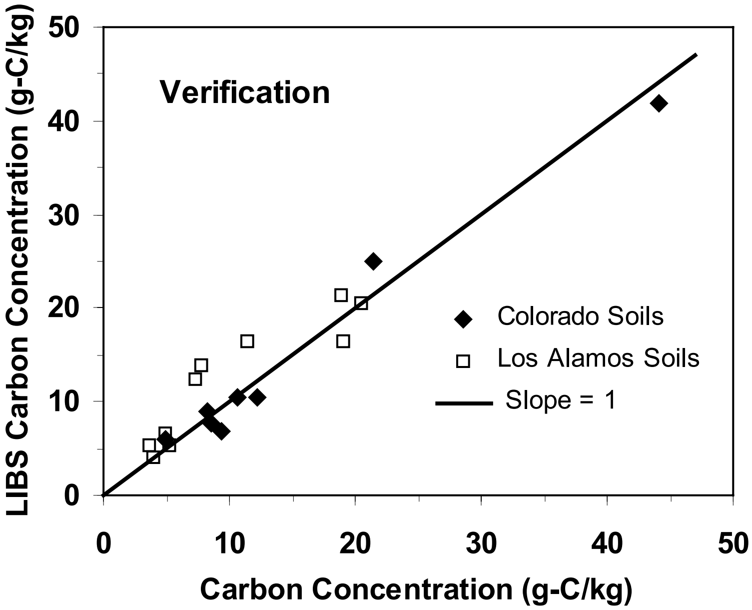

Figure 2. Carbon predicted by LIBS and measured by dry combustion from Colorado and Los Alamos soils.