SANDIA REPORT

SAND2013-1679

Unlimited Release

Printed March 2013

Monitoring Changes in Soil Carbon Resulting From Intensive Production, a Non-Traditional Agricultural Methodology

Brian P. Dwyer

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.osti.gov/bridge>

Available to the public from

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>

SAND2013-1679
Unlimited Release
Printed March 2013

Monitoring Changes in Soil Carbon Resulting From Intensive Production, a Non-Traditional Agricultural Methodology

Brian P. Dwyer
Geotechnology and Engineering Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0754

Abstract

New Mexico State University and a group of New Mexico farmers are evaluating an innovative agricultural technique they call Intensive Production (IP). In contrast to conventional agricultural practice, IP uses intercropping, green fallowing, application of soil amendments and soil microbial inocula to sequester carbon as plant biomass, resulting in improved soil quality. Sandia National Laboratories role was to identify a non-invasive, cost effective technology to monitor soil carbon changes. A technological review indicated that Laser Induced Breakdown Spectroscopy (LIBS) best met the farmers' objectives. Sandia partnered with Los Alamos National Laboratory (LANL) to analyze farmers' test plots using a portable LIBS developed at LANL. Real-time LIBS field sample analysis was conducted and grab samples were collected for laboratory comparison. The field and laboratory results correlated well implying the strong potential for LIBS as an economical field scale analytical tool for analysis of elements such as carbon, nitrogen, and phosphate.

ACKNOWLEDGMENTS

We greatly appreciate the assistance and funding from Leigh Schutzberger and the New Mexico Small Business Assistance (NMSBA) Program.

CONTENTS

Abstract.....	3
Acknowledgments.....	4
Contents	5
Figures.....	5
1. Introduction	7
2. Potential Economic Impact of Agricultural Carbon Sequestration	7
3. Potential Technologies for Soil Carbon Monitoring	8
4. Laser-induced breakdown spectroscopy- libs	9
4.1. LIBS Systems.....	9
4.2. Phase I, Laboratory Testing	10
4.3. Phase II, Field Testing of LIBS	11
5. Conclusions/recommendations.....	12
6. References	12
Distribution	14

FIGURES

Figure 1. James E. Barefield, II is shown using the Backpack LIBS system at a test site in Arizona as part of the field work completed for the ChemCam instrument on the Mars Rover Curiosity.....	9
Figure 2. Normalized integrated area of the carbon emission line at 247.856nm using the LIBS backpack unit.	11
Figure 3. Normalized integrated area of the carbon emission line at 247.856nm using the medium resolution LIBS system.....	11

1. INTRODUCTION

Members of the Institute for Sustainable Agricultural Research (ISAR) at New Mexico State University (NMSU) have been working for years on developing and applying new technologies to enhance management and operations of field and orchard crops. The primary focus is to increase grower's income, not just for a year, but for the long term. This requires a sustainable approach called Intensive Production (IP). The objectives of IP are:

1. Increasing sustainable soil fertility;
2. Tracking soil sustainable fertility;
3. Identifying technologies to assist with monitoring soil changes;
4. Evaluating bacteria and archaea DNA for Nitrogen Cycle Activity;
5. Stress evaluation over large land masses; and
6. Carbon sequestration. [3]

Sustainable agriculture is on the verge of acceptance into the whole mainstream agriculture community because it utilizes a synergistic approach toward removing C from the atmosphere while simultaneously improving soil fertility. The potential for additional revenue by sequestering carbon into soil for growers is very high.

2. POTENTIAL ECONOMIC IMPACT OF AGRICULTURAL CARBON SEQUESTRATION

Agricultural sequestration of C is a competitive approach to geo-sequestration Carbon Capture and Storage (CCS) methods. The International Energy Agency (IEA) estimates CCS technology will cost approximately \$80/ton CO₂ for capture alone. This cost does not include transportation and long term storage costs. IP sequestration of CO₂ will produce a new commodity and income source for farmers while offering a viable alternative to CCS at a fraction of the cost. Current research indicates agriculture is capable of capturing from 40-60 tons CO₂/acre/year providing long term and safe storage at pricing of <\$17/ ton CO₂. [4]

A thorough assessment of agricultural C sequestration in New Mexico alone indicates this will be a half a billion dollar industry for just the greater than 25K ton CO₂ emitters, all on only 10% of the agricultural field-crop land in New Mexico. This will offer agricultural professionals a new commodity with potential profits of \$150/Acre for one cover crop. This pricing is currently one-fifth the cost of the "capture only" portion for "CCS" technologies. There are no tool-up expenses; no catastrophic leakage liabilities and the approach offers soil fertility improvement, improved crop performance and elimination of downstream environmental pollution from run-off nutrients as another benefit. This all results in a net 5% surcharge for any energy product: \$0.006/kWh, \$0.16/gallon gasoline, \$0.18/gallon diesel etc. [4]

Expansion and acceptance of current research to support initial findings is needed to demonstrate a sound and scientific basis for further acceptance of the agricultural C-sequestration methodology. More specifically, the small business farmers need technological support to validate/verify the agricultural C-sequestration approach. The form and quantities of carbon must be measured using industry acceptable techniques.

3. POTENTIAL TECHNOLOGIES FOR SOIL CARBON MONITORING

In response to the request, SNL evaluated state of the art technologies within the laboratory complex and the commercial sector that had the potential to meet the grower's criteria. Below is a list of the SNL technologies considered.

1. SNL has recently developed/enhanced remote sensing capability and the accompanying algorithms for assessing changes in algal communities in ponds. This capability could be adapted to assess baseline vegetative cover and changes over time to support the proposed Terrestrial Carbon sequestration project.
2. SNL has a developed mobile laboratory capability in the form of two temperature controlled 30 ft. trucks with the following pertinent capability to assist this project:
  - a. Mobile platform;
  - b. Instruments for real-time GHG (greenhouse gas) measurement – aerodyne high-precision, fast CO₂ isotope analyzer, Picarro CO₂, CH₄, and H₂O analyzer;
  - c. Eddy covariance flux system – Licor NDIR CO₂ analyzer;
  - d. Picarro CO₂, CH₄, and H₂O gas analyzer;
  - e. Picarro CO₂ carbon isotope analyzer.

Next, commercially available technologies were evaluated against the criteria. The following is a list of private sector technologies reviewed:

1. Inelastic neutron scattering (INS)
2. Nuclear magnetic resonance (NMR)
3. Invasive soil sampling techniques
4. Near infra-red (NIR)
5. Mid infra-red (MIR)
6. Laser induced breakdown spectroscopy (LIBS)

LIBS was chosen as the favorable technology to meet the project intent for further review. The decision was based on maturity level, relatively low cost, and simplicity. Further investigation identified a LIBS system developed for space applications (MARS Rover attachment) at Los Alamos National Laboratory (LANL).

James E. Barefield, II and a team of researchers at LANL have developed a laser-induced breakdown spectroscopy (LIBS) backpack unit which can be used to determine the elemental composition of samples, including soils, in a field setting. James and several of his colleagues teamed with SNL to conduct laboratory and field sampling and analyses of soil located on the growers' farms near Las Cruces, NM.

4. LASER-INDUCED BREAKDOWN SPECTROSCOPY- LIBS

4.1. LIBS Systems

In laser-induced breakdown spectroscopy (LIBS), a focused laser pulse is used to generate a plasma on a sample's surface. The plasma atomizes, excites, and ionizes the sample within the laser focal volume. Once the plasma cools, the excited atoms relax to their ground states, emitting light that is unique to each element in the periodic table. The emitted light is collected and used to identify the elemental composition of the sample. The main benefit of LIBS is the rapid and real time analysis of samples in a field setting. Sample collection, packaging, and shipment of samples are not required and there is little to no sample preparation needed. In most cases, samples of interest are simply placed on the sample holder (or in the sampling chamber) and analyzed. [1]

LANL has two LIBS systems available; (1) a Backpack LIBS System, and (2) a Cart/ Rack mounted Medium Resolution LIBS System. The Backpack LIBS system consists of a Nd:YAG (Kigre, Inc) laser operating at 1/3 Hz (pulses per second) with an output energy of 25mJ/pulse, an Avantes spectrometer (resolution of ~ 2000), and a computer for system control, data acquisition, and analysis. Figure 1 shows a version the Backpack LIBS system while on deployment at a test site in Arizona. [1]

Figure 1. James E. Barefield, II is shown using the Backpack LIBS system at a test site in Arizona as part of the field work completed for the ChemCam instrument on the Mars Rover Curiosity

The second LIBS system is a Cart/ Rack mounted Medium Resolution LIBS System consisting of a Nd:YAG laser (Quantel) operating at 20 Hz with a maximum output energy of 100 mJ/pulse, an Echelle 4000 LLA Instruments spectrometer (resolution $\sim 20,000$) and a computer for system control, data acquisition and analysis. The Cart/ Rack mounted Medium Resolution

LIBS System can be made field deployable in either a truck or packaged for use in a temporary tent laboratory site since it only requires a 110V power supply source. The reason for using two different LIBS systems with different resolution spectrometers is to determine whether or not there are too many spectral features (atomic emission lines) that overlap or are contained within the same peak within the low resolution data making quantification extremely difficult. [1]

In 2012, LANL and SNL personnel collected soil samples (35) from several plots previously obtained by NMSU researchers working with the growers. The samples were analyzed in the laboratory at LANL using LIBS. Two LIBS systems were used for the analysis: the LIBS backpack unit (low resolution spectrograph) and a medium resolution LIBS system. The carbon content of the 35 soil samples were unknown to both NMSU and LANL at the time of analysis (NMSU had sent out the samples to an analytical laboratory for analysis but had not yet received the results). [1]

4.2. Phase I, Laboratory Testing

During the laboratory based preliminary testing of the soil samples, both LIBS systems (described above) were evaluated for the potential use as in-field analysis instruments. The instruments were evaluated for the rapid and accurate identification of carbon. Each soil sample was prepared in two different ways: (1) pressed into a pellet at 35,000 psi for 5 minutes and (2) transferred into small aluminum containers to simulate the actual sample conditions in the field (loose soil). The samples were analyzed without any prior knowledge of the composition of the soil (blind test). Figures 2 and 3 below show the average, normalized-integrated area for the emission line of neutral carbon (C I) at 247.865 nm from the different soil samples obtained from several farms near Las Cruces, New Mexico. The gray bars represent the data obtained with the Backpack LIBS system while the red bars represent the results from the Cart/ Rack mounted Medium Resolution LIBS System. The data shows variations in carbon content that is comparable between both LIBS systems. After the results were compiled, we were informed that the GAR sample in fact had the most organic matter (carbon content) while the others had fairly similar carbon content, validating the preliminary LIBS results. In the LIBS spectrum of soil, the carbon emission line is very close to an iron emission line. If there was not sufficient resolution to separate the spectral features, the carbon content would be difficult to accurately determine. Therefore, consistency between both LIBS instruments was critical in determining if the backpack LIBS unit had sufficient resolution for this application. Although the overall normalized integrated areas of the carbon line are different, the overall trend between the soil samples is the same. Once NMSU received the results of the soil analysis from the analytical laboratory, they confirmed the LANL LIBS results. [2]

The laboratory soil analysis results suggested the potential of LIBS for in-field analysis of soil samples that vary in carbon content. Consequently, a second project phase to include field analysis was planned.

Figure 2. Normalized integrated area of the carbon emission line at 247.856nm using the LIBS backpack unit.

Figure 3. Normalized integrated area of the carbon emission line at 247.856nm using the medium resolution LIBS system.

4.3. Phase II, Field Testing of LIBS

Following success in Phase I, a second test phase was conducted. Phase II involved deployment of the backpack LIBS unit at the various growers agricultural test plots for field measurements.

The farmers' test plots vary significantly in soil composition, moisture content and surface density/hardness. The variation exists between the different farms and more importantly within each test plot. On a test plot that may be 100 yards in length, the soil can vary from sand to clay based on the deposition history and development of the farms.

Elemental analysis of soil composition is a new application for LIBS technology; however, LIBS is well suited for this need. The level of soil organic matter (SOM) is important for sustainable agriculture minimizing fertilizer and water use. IP focuses on increasing SOM; however, acceptance of this change needs to be documented in a low cost, simple way to validate soil improvements. LIBS can provide a non-invasive method to target the primary elements of concern such as carbon, nitrogen, phosphate and other minerals. Prior to LIBS, soil samples had to be collected, packaged, and shipped to accredited analytical chemistry laboratories for analysis. This is time consuming, costly and the test results can take months to receive. Farmers need a quantitative analysis in real time that can provide rapid feedback on watering, fertilizing and changes in SOM to improve the IP process. Real time analysis using LIBS can provide the necessary feedback to the farmer within minutes to determine the presence of C, N, Ca, Mg, and Fe, to assist with the management of the farm. The rapid feedback will translate into operational cost savings and optimum management of plants to improve farmers' profit margins. In addition, LIBS can provide an industry acceptable method to verify carbon changes in soil facilitating farmers looking to participate in the carbon sequestration arena.

5. CONCLUSIONS/RECOMMENDATIONS

The Phase II field test results show the potential of LIBS for in-field analysis of carbon content in varied soil samples. Phase III, sample locations within the farmers' test plots, should be identified by GPS location. Field sample analysis using LIBS should then be conducted on a semiannual or annual basis, as funding allows, to assess changes over time in soil elements. The analysis should also be expanded to include nitrogen and other elements of interest. The final task of Phase III should be the development of elemental calibration curves for quantitative or semi-quantitative analysis of the soils. Finally, deploying the Backpack LIBS and the Cart/Rack mounted Medium Resolution LIBS System to farms near Las Cruces, New Mexico for in-field soil analysis would allow for the determination of the robustness of the instruments under field conditions including temperature, humidity, and sample composition.

6. REFERENCES

1. Barefield II, James E., "Backpack LIBS: Laser-Induced Breakdown Spectroscopy," in 2012 R&D 100 Entry, LA-UR-12-01449, Los Alamos National Laboratory (2012).
2. Barefield II, James E., and Judge, Elizabeth J., Chemical Diagnostics and Engineering MS J565, Chemistry Division, Los Alamos National Laboratory. "Applications of Laser-Induced Breakdown Spectroscopy (LIBS) to In-Field Soil Analysis for Sustainable Agriculture", A summary New Mexico Small Business Report. 2012.

3. Ellington, Joe, Program Director. Professor of Entomology, Institute for Sustainable Agricultural Research (ISAR), New Mexico State University. Las Cruces, NM 88003. "A Technologically Advanced System (TAS) for the Analysis of Agricultural Cropping Systems Using Intense Sustainable Agricultural Practices (ISAP).
4. Johnson, David. Co-Program Director Institute for Sustainable Agricultural Research (ISAR), New Mexico State University. "Personal communications", 2012.

DISTRIBUTION

External (Electronic Copy)

- 1 Wes Eaton
777 Abbey Rd.
Las Cruces, NM 88005
weaton@nmsu.edu
- 1 Dosi Alvarez
1049 Mercantil Ave.
La Union, NM 88021
Lazy_a@msu.com
- 1 Keith Deputy
6263 Westside Dr.
Canutillo, TX
Altennis21@hotmail.com
- 1 Joe Ellington
Professor of Entomology
College of Agricultural, Consumer and Environmental Sciences
MSC 3BE
New Mexico State University
P.O. Box 30003
Las Cruces, NM 88003-8003
jelling@nmsu.edu
- 1 David Johnson
MSC WERC
New Mexico State University
P.O. Box 30001
Las Cruces, NM 88003-8001
johnsoda@nmsu.edu
- 1 James E. Barefield II, Ph.D
Chemical Diagnostics and Engineering
Los Alamos National Laboratory
Mail Stop J565
Los Alamos, NM 87545
jbarefield@lanl.gov

1 Beth J. Judge, Ph.D
Chemical Diagnostics and Engineering
Los Alamos National Laboratory
Mail Stop J565
Los Alamos, NM 87545
bethjudge@lanl.gov

Internal (Electronic Copy)

1	MS0754	D. Borns	6912
1	MS0754	B. Dwyer	6912
1	MS1495	L. Schutzberger	1933
1	MS0899	Technical Library	9536