Final report of the project "Laserperusteinen maaperän hiilivaraston nopea määritys"

1. Presentation of the project

1.1. Basic information about the project

Project name:	Laser-based soil carbon monitoring Laserperusteinen maaperän hiilivaraston nopea määritys
Principal Investigator:	Prof. Juha Toivonen Department of Physics, Tampere University (TAU)
Project duration:	1st May 2021 – 30th September 2023

1.2. Project objectives

A reliable and rapid measurement method is a pre-requisite to encourage carbon sequestration and to develop farming practices, verification, and large-scale monitoring of the soil carbon content. Also, soil carbon measurement is a crucial component in the context of carbon markets and agricultural subsidies. Measuring soil carbon content with current laboratory-based methods is labor-intensive, costly, and time-consuming, posing a challenge for large scale soil carbon monitoring.

In this project, our aim was to develop a laser-based method based on the principle of laser-induced breakdown spectroscopy (LIBS) for rapid on-site determination of soil carbon content. Utilization of LIBS enable construction of a simple and compact prototype device that can be used for obtaining quantitative compositional information and with minimal sample treatment. The main goals of the project were the following:

1. Optimization of LIBS measurement parameters to determine soil carbon content
2. Study of LIBS spectral response of carbon to different soil samples
3. Construction of field-ready measuring device
4. Field demonstration of the LIBS method for assessing soil carbon content
5. Presentation of the measurement method to domestic and international research communities

1.3. Summary of the project

The subject of the project was to develop a field capable optical soil carbon assessment method. The technical development of the Laser-Induced Breakdown Spectroscopy (LIBS) -based method was carried out in the premises of Photonics Laboratory at Tampere University (TAU). The TAU located persons involved in the project are listed in Table 1.

Table 1. TAU personnel participated in the project

Prof. Juha Toivonen	Principal Investigator
Dr. Vishal Dwivedi	Researcher
Dr. Jan Viljanen	Researcher
Dr. Piotr Ryczkowski	Staff Scientist
Dr. Mohammad Bitarafan	Researcher
Dr. Nikita Kikilich	Researcher
M.Sc. Abba Saleh	Researcher
Joni Ahokas	Master student
Thu Hoang	Research assistant
Emma Vilenius	Research assistant
Aarni Akkala	Research assistant
Maria Fabritius	Research assistant
Tuomas Seppä	Mechanical workshop
Tommi Salo	Mechanical workshop

The project involved numerous collaborations that included sample, resource, and information sharing. The main collaborators are listed in Table 2.

Table 2. Collaborators and their roles

Prof. Jari Liski	Finnish Meteorological Institute, Carbon Action	Co-ordination, contacts, and measurement sites
Prof. Jussi Heinonsalo	University of Helsinki	Samples and reference data
Dr. Narasinha Shurpali	Institute of Natural Resources Finland (LUKE)	Samples and reference data
Dr. Visa Nuutinen	Institute of Natural Resources Finland (LUKE)	Samples and reference data
Dr. Ilkka Herlin	Qvidja farm	Development of soil drill for sampling purposes

Table 3. Budget of the project

	Total
Salaries	154 917 €
Direct side costs	69 713 €
Overhead costs	213 398 €
Consumables	46 115 €
Services	12 000 €
Travel costs	11 000 €
Total	507 143 €
Funding MMM (70%)	355 000 €
Self-funding (30 %)	152 143 €

Table 3 shows the budget of the project where MMM funding covers in total of 355 000 € of the project costs. The costs of the project was reported in two periods and the realized costs are shown in the Table 4 and Table 5.

Table 4. Costs of the project 1.4.2021-31.10.2022

	Rahoitus-hakemuksessa esitetty kustannusarvio hankkeelle	Aiemmin raportoidut kustannukset	Haettavat toteutuneet kustannukset	Kustannukset yhteensä	Kustannusarvion ja toteutuneiden kustannusten erotus
Palkat	154822.00		52026.70	52026.70	102795.30
Henkilösivukulut	69670.00		23411.99	23411.99	46258.01
Palkkiot				0.00	
Matkakulut	11000.00		19050.84	19050.84	-8050.84
Ostopalvelut	12000.00		1881.33	1881.33	10118.67
Muut kustannukset yhteensä, josta	259651.00		85901.26	85901.26	173749.74
- julkaisukustannukset					
- tarvikkeet	46384.00		9246.54	9246.54	37137.46
- laitteet			4967.96	4967.96	-4967.96
- yleiskustannukset	213267.00		71666.76	71666.76	141600.24
- muut kustannukset			20.00	20.00	-20.00
Arvonlisävero yhteensä			0.00		
-10%					
-14%					
-24%					
YHTEENSÄ, josta	**507143.00**		**182272.12**	182272.12	324870.88
MMM:n rahoitusosuus	**355000.00**		**127590.48**	127590.48	227409.52
Muu rahoitus					
Omarahoitusosuus	**152143.00**		**54681.64**	54681.64	97461.36

Table 5. Costs of the project 1.11.2022 - 30.09.2023

	Rahoitus-hakemuksessa esitetty kustannusarvio hankkeelle	Aiemmin raportoidut kustannukset	Haettavat toteutuneet kustannukset	Kustannukset yhteensä	Kustannusarvion ja toteutuneiden kustannusten erotus
Palkat	154822,00	52026,70	105136,04	157162,74	-2340,74
Henkilösivukulut	69670,00	23411,99	47311,30	70723,29	-1053,29
Palkkiot				0,00	
Matkakulut	11000,00	19050,84	12089,45	31140,29	-20140,29
Ostopalvelut	12000,00	1881,33	263,00	2144,33	9855,67
Muut kustannukset yhteensä, josta	259651,00	85901,26	167602,69	253503,95	6147,05
- julkaisukustannukset					
- tarvikkeet	46384,00	9246,54	16321,94	25568,48	20815,52
- laitteet		4967,96	1324,34	6292,30	-6292,30
- yleiskustannukset	213267,00	71666,76	144825,00	216491,76	-3224,76
- muut kustannukset		20,00	5131,41	5151,41	-5151,41
Arvonlisävero yhteensä		0,00	0,00		
-10 %					
-14 %					
-24 %					
YHTEENSÄ, josta	**507143,00**	**182272,12**	**332402,48**	514674,60	-7531,60
MMM:n rahoitusosuus	**355000,00**	**127590,48**	**227409,52**	355000,00	0,00
Muu rahoitus					
Omarahoitusosuus	**152143,00**	**54681,64**	**104992,96**	159674,60	-7531,60

Description of projects outcome per objectives

Optimization of LIBS measurement parameters to determine soil carbon utilizing an existing laboratory-based LIBS setup

In this phase, we have used our existing resources and expertise at TAU, to optimize critical experimental parameters, including laser parameters (energy, wavelength, frequency, etc.), signal acquisition parameters (delay time and exposure time), number of measurements required per sample, and other relevant factors. Figure 1(a) shows an example for the optimization of the laser energy per pulse, while Figure 1(b) shows the optimization of the acquisition delay time. The figures demonstrate that as the energy increases, the signal also increases, but if the acquisition is delayed, the signal begins to decline. Hence, achieving a sufficiently robust signal requires careful optimization of these parameters. We have performed an extensive series of measurements to optimize all the necessary parameters.

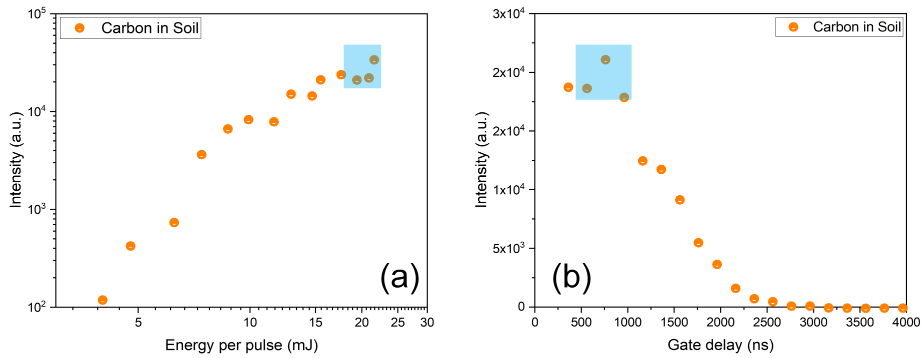

Figure 1: (a) An example for the optimization of the laser energy per pulse and (b) the optimization of the acquisition delay time.

Study of LIBS spectral response of carbon to different soil samples

In this phase, soil sampling was designed considering the factors such as soil heterogeneity and variability in the field. In our practice we have designed a systematic procedure to handle soil samples and preparing circular pellets (diameter 30 mm and thickness 5 mm) from the real samples. Various samples have been tested and spectral response of carbon were recorded. Figure 2 shows an example of carbon spectral line at 193.1 nm and neighboring Al (ionic) spectral line at 193.5 nm from a top-soil (0-10 cm) sample.

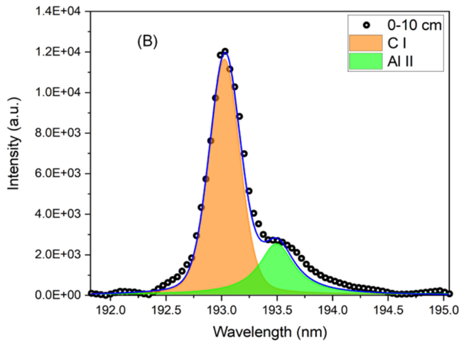

Figure 2: An example of carbon spectral line at 193.1 nm

Design and construction of field-ready measuring device

In this phase of the project, we have successfully designed and developed a field-capable device with an overall dimension of 60 cm × 45 cm × 19 cm (length × width × height) in the form of a closed box. The samples are placed inside the device by accessing the provided hatch. The device is powered by a battery and all the controls of the device are managed through a custom in-house designed LabVIEW-based interface. The details of the used components are reported in the publication (Dwivedi *et al.*, Geoderma, 2023). Figure 3 shows the photograph of the device mounted on a mobile table-top and powered by a battery. Figure 3 also shows the actual optical configuration of the device and a photograph showcasing the laser craters on a standard copper sample used for testing.

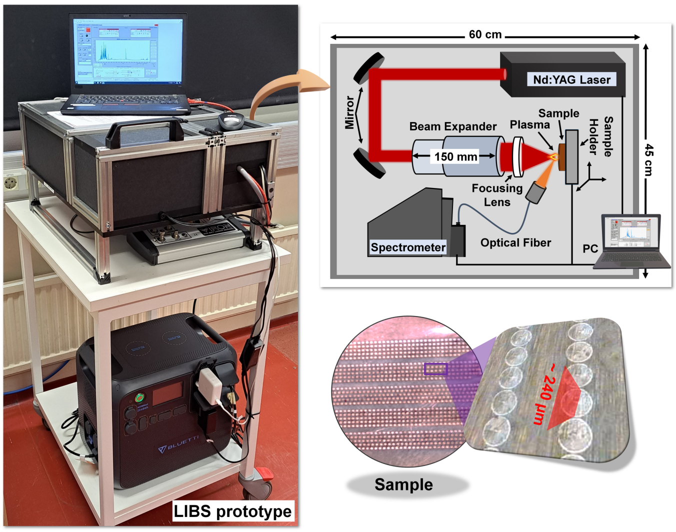

Figure 3: A photograph of the prototype device mounted on a mobile table-top, the actual optical configuration of the device and a photograph of LIBS measured standard copper sample.

Field demonstration of the LIBS method for assessing soil carbon content

After rigorous testing of the device and successful laboratory-based measurement campaign, we have moved the device to various agricultural sites (Carbon Action collaboration) for on-site measurements. We have developed a measurement protocol and a simplified user manual for the device. With the current configuration, individuals without specialized expertise can operate the device after a short training session. Furthermore, there is potential for enhancing the device's user-friendliness, but achieving this would necessitate additional research, time, and resources.

Figure 4: A photograph of Carbon LIBS device during on-site measurements at Qvidja farm, Finland

Presentation of the measurement method to domestic and international research communities

We have shared our research with diverse communities, including farmers, soil scientists, and decision makers. These demonstrations have provided us with valuable feedbacks that will be taken into account in our forthcoming related research activities. The results and outcomes of the project were also presented to research communities in various national and international conferences.

2. Project implementation and evaluation of the implementation phase

2.1. Methodology and material

The main methods and materials and implementation arrangements (e.g. literature study, field trials, laboratory tests, etc.) are briefly described.

Within the project, we employed a spectroscopy-based method known as LIBS. We have surveyed dozens of scientific articles using TAU library resources, concerning the elemental analysis of soil using the LIBS technique and have narrowed our focus to soil carbon analysis in particular. From the study, it was revealed that the selection of appropriate experimental parameters and components is vital to the success of such analyses. Also, sample handling in case of soil samples plays a significant role. Those factors were carefully considered throughout the project.

The components used in the development of the finalized device are reported in the publication. However, many other optical, optomechanical, electronic, or other components have been used for various testing, research, and development purposes.

The laboratory testing of the device entailed measuring hundreds of soil samples obtained from various agricultural fields in Finland, at the laboratory of TAU. At this stage, we have checked the power consumption of the device, laser safety, and the stability and reproducibility of the measurements. Field trials and demonstration were conducted at Qvidja agricultural field, Finland, under carbon action collaboration.

2.2. Schedule and resources (incl. implementation organisation and partners)

The project partners and their role in the implementation of the project. Who was responsible for which sub-task, what cooperation was carried out, what were the main experiences (good/bad), possible suggestions for improving cooperation in the future, etc.

All the instrument and device development related work have been performed by the members of Applied Optics group of TAU led by Prof. Juha Toivonen. The group has many years of experience in developing devices for various environmental sensing applications and special expertise on LIBS technique. Therefore, the sub tasks were divided among the students and the members of group and were executed in a timely manner. Resources from Photonics laboratory and the library of TAU have been used during the execution of the project. Other than TAU resources, carbon action collaboration was used for assessing soil samples and agricultural sites.

2.3. Costs and funding

The project costs and funding were already summarized in Chapter 1.3 in Table 3, Table 4, and Table 5. Please see that part of the report for project costs and budgeted funding.

2.4. Reporting, publications and monitoring

TAU project page summarizes the objectives of the project and contains links to key results of the project. https://research.tuni.fi/applied-optics/projects/carbonlibs/

Further reporting has been done in forms of publication, conference presentations, and master of science thesis. These are listed in below.

Publication

V. Dwivedi, J. Ahokas, J. Viljanen, P. Ryczkowski, N.J. Shurpali, H.R. Bhattarai, P. Virkajarvi, J. Toivonen, Optical assessment of the spatial variation in total soil carbon using laser-induced breakdown spectroscopy, Geoderma 436 (2023), 116550, https://doi.org/10.1016/j.geoderma.2023.116550.

Presentations at conferences

1. Vishal Dwivedi et al.: LIBS-based multi-elemental analysis of agricultural soil, 19th European Winter Conference on Plasma Spectrochemistry, Ljubljana, Slovenia 29.1. – 3.2.2023
2. Vishal Dwivedi et al.: Total Soil Carbon Assessment Using Laser-Induced Breakdown Spectroscopy, Optics and Photonics Days (OPD2023), Joensuu, Finland 30.5. – 1.6.2023)
3. Vishal Dwivedi et al.: Development of a Field-Capable LIBS System for Rapid Soil Elemental Monitoring, 12th Euro-Mediterranean Symposium on Laser-induced Breakdown Spectroscopy, Porto, Portugal, (September 04-07, 2023)
4. Jan Viljanen, Vishal Dwivedi et al.: Total soil carbon assessment using LIBS, Northern European 4 per 1000 meeting, Helsinki, Finland, (June 06-08, 2023)
5. Thu Hoang et al.: Moisture calibration in laser-based elemental analysis of soil, OPD2023
6. Joni Ahokas et al.: Environmental sensing with laser-induced breakdown spectroscopy, Optics and Photonics Days (OPD2023), Joensuu, Finland 30.5. – 1.6.2023
7. Joni Ahokas et al.: Monitoring Soil Carbon Distribution Using Laser-Induced Breakdown Spectroscopy, Optica Sensing conference, Vancouver, Canada 10.7. - 15.7.2022
8. Joni Ahokas at el.: Monitoring Soil Carbon Distribution Using Laser-Induced Breakdown Spectroscopy, XII World Conference On Laser Induced Breakdown Spectroscopy, Bari, September 5-9, 2022
9. Joni Ahokas et al.: Environmental sensing with laser-induced breakdown spectroscopy, The 49th European Conference on Plasma Physics, Bordeaux, France from 03.07.2023 - 07.07.2023

Master of science thesis

Joni Ahokas (2023): Soil Carbon Monitoring Using Laser-Induced Breakdown Spectroscopy

2.5. Evaluation of the implementation phase

All the objectives of the project have been successfully achieved. We developed a totally new technology for rapid soil carbon analysis in this project. The task was made possible by utilizing various optical, electrical, and mechanical skills of employees of Tampere University. We also visited several conferences to learn state of the art knowledge in the technology area and utilized the gathered information efficiently into practical implementation of a demonstration device for the new technology. At the last summer of the project in 2023 we were demonstrating the technology at various domestic sites and conferences. However, to deploy the technology more widely at the fields, more on-site testing is required to understand and address issues that arise during the transition from a laboratory setting to a field environment. Achieving this ambitious goal would necessitate additional research, time, and resources in future projects.

3. Results and their evaluation

3.1. Presentation of results

In this project, we have developed a compact and robust LIBS device that can be easily transported to the fields for on-site soil analysis. Further, we have presented a calibration model for quantification of total soil carbon that can be applied to obtain 3D spatial variation of total soil carbon in the field. The robustness of the calibration model was demonstrated by comparing the LIBS method calibration to fresh and unprocessed samples from two different fields of similar soil type but from different geographical locations as the field used for calibration. The global relative uncertainty in LIBS results was found to be about ± 10 %, which may be attributed to soil matrix differences, soil properties, e.g., types, structure, and morphology, and the inaccuracy of dry combustion measurements in addition to normal statistical variation from LIBS.

With our device, we have measured 175 mineral soil samples collected from ten different depths (0-97 cm) and 28 different locations from a 6.3 ha agricultural field, AN (63°09′49′′ N, 27°14′3′′ E) located in Maaninka region in eastern Finland, in order to access total amount of soil carbon. We have calibrated LIBS signal against standard dry combustion method using a randomly selected small set of samples (total 8) and validated using additional 167 samples (with carbon content ranging from 1 to 85 $g \cdot kg^{-1}$) from the different locations of the same field. With those measurements, we have demonstrated 3D spatial variation of total soil carbon in the test field (Figure 5). The robustness of the calibration model was demonstrated by comparing the LIBS method calibration to fresh and unprocessed samples from two different fields of similar soil type but from different geographical locations as the field used for calibration. The global relative uncertainty in LIBS results was found to be about ±10 %, which may be attributed to soil matrix differences, soil properties, e.g., types, structure, and morphology, and the inaccuracy of dry combustion measurements in addition to normal statistical variation from LIBS. The specifics regarding the soil samples and the LIBS results have been documented and published in an open-access scientific journal (Dwivedi *et al.*, Geoderma, 2023).

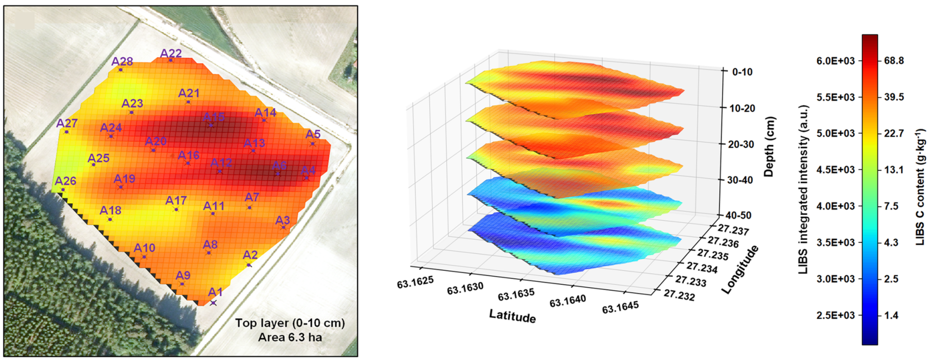

Figure 5: Spatial variation of total soil carbon in the test field (AN).

Publication

V. Dwivedi, J. Ahokas, J. Viljanen, P. Ryczkowski, N.J. Shurpali, H.R. Bhattarai, P. Virkajarvi, J. Toivonen, Optical assessment of the spatial variation in total soil carbon using laser-induced breakdown spectroscopy, Geoderma 436 (2023), 116550, https://doi.org/10.1016/j.geoderma.2023.116550.

3.2. Putting results into practice

In comparison to current methods, the LIBS analysis is simple and fast, with measurement time of only about one minute per sample. In addition, LIBS analysis can be performed on-site reducing the need of soil storage capacity and, as the calibration for a field block can be obtained from a small number of samples, the sample handling in laboratory is reduced substantially. Hence, LIBS enables spatial and temporal frequent carbon monitoring without extensive laboratory work and has the potential to become part of the future carbon monitoring network in Finland and internationally. A fast and reliable method to measure soil carbon enables an incentive for carbon farming in the form of agricultural support. With this, agricultural carbon emissions can be reduced and even produce negative carbon emissions. Additionally, understanding how carbon behaves in the soil helps make climate predictions more accurate, which is essential for planning actions to address climate change.

Although there have been significant advancements in the field of LIBS instrumentation on a global scale, a ready to use device for conducting on-site soil carbon measurements is still not available. While we have conducted preliminary on-site measurements (in collaboration with carbon action partners) using our device and results are promising, it is evident that further progress and research is required to automate the entire measurement process.

The results we have obtained offer a preliminary step and foundational information for those considering the development of a new business. The possible paths for the commercialization of the method can be explored with established companies. The results are directly benefiting to the farmers, authorities, policymakers, who have a vested interest in soil carbon monitoring. We have presented the results in different national and international conferences to multi-dimensional research community, and also to the end users at farms.

3.3. Relevance of results and follow-up

While several international research groups have utilized the LIBS method for soil elemental and carbon analysis, the diverse nature of soil presents numerous challenges as reported in the literature. There have been no prior attempts at on-site large-scale LIBS soil carbon monitoring. We have developed a systematic protocol for soil sample handling and field capable LIBS device for obtaining on-site soil carbon content and we have already performed field tests. In addition, LIBS method is able to offer simultaneous multi-elemental detection, our device can also be used for the investigation of the elements in soil beyond C, like nitrogen and phosphorus. Also, through the application of machine learning techniques, harnessed to derive additional soil characteristics such as soil type, pH, etc. Additionally, as the next phase of our plan, we intend to conduct measurements directly on soil drill cores, streamlining the process by reducing the sample handling steps and speeding up the measurements. Depending on the resources, we will continue to further advance research and development of the LIBS device for soil carbon measurements in field conditions. Future resources should be directed to enable wider usage of the rapid soil carbon analysis together with soil modelling to build comprehensive monitoring of soil carbon content.