



## Review

# Laser-induced breakdown spectroscopy (LIBS) to measure quantitatively soil carbon with emphasis on soil organic carbon. A review



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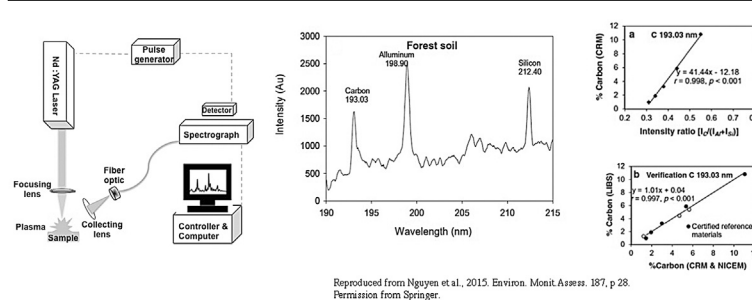
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## HIGHLIGHTS

- Soil C measurement is a crucial factor for quantifying and monitoring soil C content.
- LIBS is a very powerful analytical technique for quantitatively measuring elements in soils.
- LIBS instrumentation, principles, and chemometric methods for C analysis are shortly reviewed.
- LIBS advantages and limitations/drawbacks are commented and final remarks and future perspectives provided.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Soil organic carbon (OC) measurement is a crucial factor for quantifying soil C pools and inventories and monitoring the inherent temporal and spatial heterogeneity and changes of soil OC content. These are relevant issues in addressing sustainable management of terrestrial OC aiming to enhance C sequestration in soil, thus mitigating the impact of increasing CO<sub>2</sub> concentration in the atmosphere and related effects on global climate change. Nowadays, dry combustion by an elemental analyzer or wet combustion by dichromate oxidation of the soil sample are the most recommended and commonly used methods for quantitative soil OC determination. However, the unanimously recognized uncertainties and limitations of these classical laborious methods have prompted research efforts focusing on the development and application of more advanced and appealing techniques and methods for the measurement of soil OC in the laboratory and possibly *in situ* in the field. Among these laser-induced breakdown spectroscopy (LIBS) has raised the highest interest for its unique advantages. After an introduction and a highlight of the LIBS basic principles, instrumentation, methodologies and supporting chemometric methods, the main body of this review provides an historical and critical overview of the developments and results obtained up-to-now by the application of LIBS to the quantitative measurement of soil C and especially OC content. A brief critical summary of LIBS advantages and limitations/drawbacks including some final remarks and future perspectives concludes this review.

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## 1. Introduction

The role of soils in the biogeochemical cycle of carbon (C) is universally recognized as being very relevant on the basis of soil capacity to store C in amounts about four times more than plants and about three times more than the atmosphere [1]. In world soils, the most part of C is present as organic C (OC) in the form of more or less complex and stable organic compounds originated from plant, animal and microbial residues, whereas the inorganic C (IC) portion is present in the form of carbonates [2]. In particular, the soil OC pool is reasonably considered to represent a major contributor in sequestering C in the terrestrial compartment and in balancing global and regional C fluxes [3–5]. Thus, in order to enhance the amount of OC stored by appropriate practices, e.g. reduced tillage, crop rotation, organic residue incorporation, improved grazing, conservation plans, etc., the correct and sustainable management of soil OC stocks is very important for the mitigation of increasing CO<sub>2</sub> concentration in the atmosphere and related impact on climate changes.

Accurate soil OC measurements are thus crucial for quantifying soil OC pools and inventories, and monitoring the inherent spatial heterogeneity of soil OC content and changes that may occur as a consequence of diverse land use and management practices [6,7]. The standard method used for measuring soil OC was for many years the traditional Walkley-Black dry combustion procedure [8] based on the measurement of emitted CO<sub>2</sub> [9] or on sample weight changes [10]. Nowadays, wet combustion by dichromate oxidation of the sample and dry combustion by an elemental analyzer are the most commonly used and recommended techniques for soil OC determination [9]. However, these classical laboratory methods feature well recognized uncertainties and limitations, are laborious and time consuming, and further complicated by the spatial and temporal OC content variability along the soil profile.

As a consequence, the development of soil sampling schemes that are repeatable and representative for large areas and of more robust, precise, accurate, rapid and cost-effective techniques and methods requiring no or minimal sample pretreatment, which can minimize uncertainties and improve estimates of terrestrial OC inventories and fluxes, is a pressing and crucial need [3,11]. The development and application of novel techniques is thus expected to allow a better quantification and verification of temporal and spatial changes of soil OC contents in addressing global climate change and terrestrial C management issues.

Starting from the beginning of this millennium, research efforts have focused on the measurement of soil C, in particular OC, *in situ*, i.e. in the field, using a variety of advanced/appealing methods,

including inelastic neutron scattering (INS) and gamma-ray spectroscopy [12,13], mid- and near-infrared diffuse reflectance spectroscopy (MIRS, NIRS, DRIFTS) [14], remote sensing imagery [15] and laser-induced breakdown spectroscopy (LIBS) [16]. Field analysis of soil C by these techniques presents several benefits, including minimal soil disturbance, high sensitivity and selectivity with no (or minimum) sample preparation, and the possibility of repetitive and sequential measurements for the evaluation of spatial and temporal C stock variations at a large scale. However, each of these techniques presents instrumental and/or procedural drawbacks and limitations. In particular, the INS technique is capable of analysing intact soil samples on a large spatial scale, but the instrumental and transport costs are high and radiological control licenses and appropriately trained technicians are required. The NIRS/DRIFTS is a nondestructive, rapid, relatively low cost and simple in operation and maintenance technique, but soil moisture and carbonate content may complicate calibration and analytical interpretations. Limited studies have been conducted on the direct measurement of soil OC content and distribution by remote sensing. Although a high correlation has been reported between soil OC content and Munsell color properties calculated from visible soil reflectance data within a landscape, serious limitations of this technique have been encountered due to soil color and reflectance dependence on many other soil physical and chemical properties, management practices and presence of vegetation and surface organic residues [17].

The objective of this review is to survey historically and critically the results obtained up-to-now by the application of LIBS to the quantitative measurement of soil C content, with emphasis on soil OC, highlighting its advantages and limitations/drawbacks. It is important to remark here that the papers reviewed below often do not specify that results refer actually to soil OC, but it is so as the calibrations are performed in all cases with respect to soil C measured by dry combustion or similar methods that actually measure soil OC.

## 2. Highlights of principles, instrumentation, methodologies and supporting chemometric methods of LIBS

LIBS is an atomic emission spectroscopy technique in which a high energy laser pulse is focused on a sample surface thus causing its ablation, evaporation, atomization and ionization, and excitation, i.e. the generation of a high-temperature plasma that must achieve the so-called Local Thermodynamic Equilibrium (LTE) state [18–22]. During relaxation excited atoms, ions and molecular fragments in the plasma emit radiations at wavelengths distinctive of the elements present in the sample under study. The emitted

light is then collected, spectrally resolved and then detected by a charge-coupled detector (CCD) or intensified (I) CCD that can delay the detection with respect to plasma formation and be gated, thus optimizing the signal-to-noise ratio of the acquired spectrum. The individual peaks in the spectrum are typical of the elements present in the sample and feature three main parameters, i.e. wavelength, intensity, and shape, which depend on the structure, surrounding environment and emitting elements amount. LIBS has been employed successfully for the qualitative and quantitative analysis of various elements in samples of diverse origin and nature including soils [23–27].

A LIBS instrument consists basically of a laser, an optical set to focus the laser, a light detection unit of the plasma, and a computer for control and data acquisition processing (Fig. 1). Among the various laser sources used in the LIBS technique, the neodymium-doped yttrium/aluminum garnet (Nd:YAG) pulsed laser operating at output wavelengths of 1064, 532, 355, 266 or 213 nm is preferred in most LIBS applications due to its reliable, compact and highly focused power density. The laser light passes through a lens that focuses the energy onto the sample placed at a few cm to am from the laser source. The laser does not blast and excite the sample by a nonstop beam, but by one or more ns-wide laser shot pulses of high-intensity each lasting about 5–20 ns. The typical energies of laser pulses in LIBS are in the range from 1 to 150 mJ, depending on the specific requirements.

In conclusion, the objective of LIBS is to obtain an optically thin plasma in the LTE state whose elemental composition is equal to that of the sample, i.e. a stoichiometric ablation can be assumed. In this condition the spectral line intensities will be related to the actual element concentrations in the sample [18]. The quantitative evaluation of emission lines in LIBS spectra is generally performed by appropriate calibration models among which partial least square regression (PLSR) [28] or projection to latent structures (PLS) [29–31] are the most used; whereas chemometric methods, e.g. principal component analysis (PCA) is used for samples classification [32] and discrimination [33]. Other, even more advanced methods and models are available to analysing LIBS data, i.e. the least absolute shrinkage and selection operator (LASSO) [34] and the sparse multivariate selection regression with covariance estimation (MRCE) [35], etc., but the treatment of these methods is out of the scope of this review.

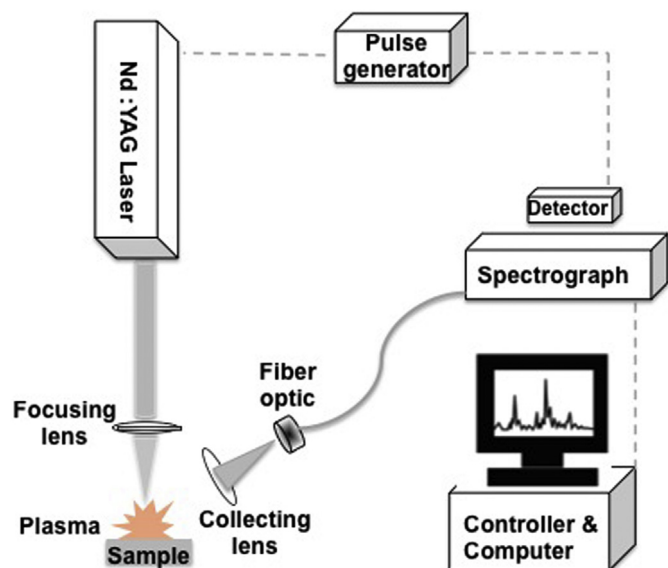


Fig. 1. Experimental scheme of a laser-induced breakdown spectroscopy (LIBS) system.

### 3. Measuring soil organic C content by LIBS

#### 3.1. Use of the C I emission line at 247.8 nm

The first application of LIBS to measure soil C content was reported by Cremers et al. [36] who used a Nd:YAG laser at a wavelength of 1064 nm on two Aridic Argiustoll, an Aridic Paleustoll and an Ustic Torriorthent from farms in Colorado and an Typic Haplustalf from a woodland in New Mexico. The strong C I emission line at 247.8 nm was selected for testing and calibrating LIBS data with those obtained by conventional dry combustion analysis. Twenty 50-mJ laser pulses of 10 ns were used for each measurement and the precision was increased by performing 6–12 replicate measurements on several samples. The ratio of LIBS C signal at 247.8 nm to the signal of Si, whose concentration was assumed to be the same in all samples, resulted highly correlated (coefficient of determination,  $r^2 = 0.96$ ) with the OC concentration measured by dry combustion. The calibration curve obtained was shown to be useful in predicting the C content of additional soil samples of different mineralogy. The LIBS detection limit was estimated to be 300 mg C kg<sup>-1</sup> with a precision of 4–5% and accuracy of 3–14%. Thus LIBS showed to be a promising technique to measure soil OC with short analysis time and acceptable detection limits, accuracy and precision. However, the effects of various soil properties, such as texture, carbonate content, range of total soil C, moisture, clay mineralogy, Si content and others, on LIBS measurements should be investigated more extensively. Further, the potential of field-portable LIBS instruments for *in situ* measurements of C in intact soil profiles should be explored in future research to broaden the applicability of LIBS analysis to soil C.

The preliminary study of Cremers et al. [36] was extended by Martin et al. [37] who used a Q-switched Nd-YAG laser at the wavelength of 266 nm with 23-mJ pulse and provided with an ICCD to measure the C and N contents of fifteen soil samples from Oak Ridge and southwest Virginia mined lands with total C concentrations ranging from 0.16% to 4.3%, which were previously acid-washed and dried. The LIBS C signal at 247.8 nm (Fig. 2) measured on 20 pellets from each homogenized soil sample was shown to be highly correlated (coefficient of determination,  $r^2 = 0.962$ ) with the OC content measured by dry combustion using an elemental analyzer (Fig. 3). The authors [37] demonstrated that the analytical reproducibility and reliability of data could be

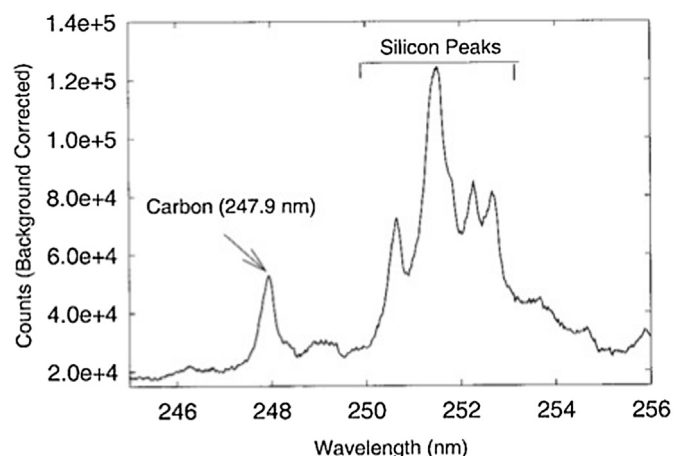


Fig. 2. LIBS spectrum for carbon in soil. Reprinted from Applied Optics, Vol. 42, M.Z. Martin et al., Laser-induced breakdown spectroscopy for the environmental determination of total carbon and nitrogen in soils, pp 2072–2077. Copyright 2003, with permission from Optical Society.

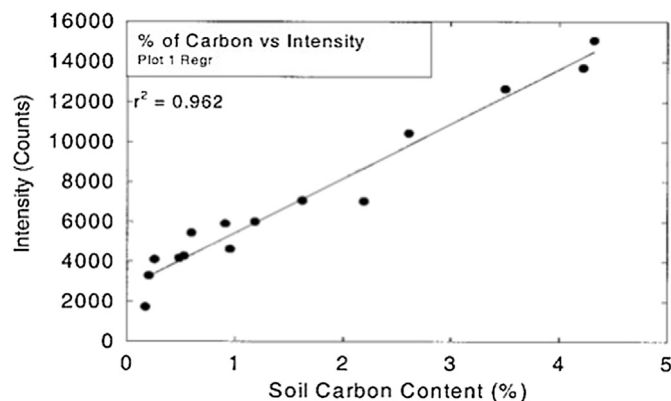


Fig. 3. LIBS signal versus soil carbon content measured with the LECO CN-analyzer. Reprinted from *Applied Optics*, Vol. 42, M.Z. Martin et al., Laser-induced breakdown spectroscopy for the environmental determination of total carbon and nitrogen in soils, pp 2072–2077. Copyright 2003, with permission from Optical Society.

improved, i.e. the standard deviation could be reduced, by three ways: (i) increasing the number of shots, i.e. 100 instead of 10 shots, and moving the pellet around to cover a large area, and then averaging the spectra obtained; (ii) using the C/Si ratio that improves the correlation between the LIBS C signal and C data from conventional analysis; and (iii) using the linear correlation method based on the theory of covariance that measures the tendency of two variables to vary together, thus suppressing the effect of signal-intensity fluctuations.

In a successive study Martin et al. [38] explored a set of operational parameters, including laser wavelength and excitation energy, and statistical analysis methods based on univariate and multivariate approaches, to develop a robust calibration model to quantify soil C concentration independently of soil chemical and physical properties. A Q-switched Nd:YAG laser at wavelengths of 1064 and 532 nm and three different excitation energies (135, 90 and 45 mJ), in comparison to a CN analyzer, was used to evaluate the C content in 38 soil samples covering the C concentration range from 0.5 to 4%, and rich in clay, sand or silt, which were collected respectively from agricultural fields in Michigan, North Dakota and Illinois at a depth of 0–5 cm. An ICCD was used to detect the resolved LIBS spectra and data were averaged for 100 laser shots. In particular, PCA and PLS (or PLRS) were applied using a software package capable to perform both. The emission lines, including the C I line at 247.8, were found to be more pronounced in the spectra acquired at 532 nm and energy of 90 mJ, whereas the C I line was obscured by the Fe line at 1064 nm and energies of 90 and 135 mJ. These results were confirmed by performing PCA on the entire spectral set, which allowed to detect clusters based on different wavelength and excitation energy combinations and showed that coupling the laser and the sample was more efficient at 532 nm than at 1064 nm, possibly due to various factors affecting the mechanism of laser-matter interaction. A univariate approach was used to construct a calibration model for each soil series and for the entire 38 sample data set by correlating the LIBS signal intensity of C I at 247.8 nm to the OC content measured by dry combustion. The model showed that, although each type of soil exhibited a different slope and intercept, the highest  $r$  value and lowest root mean square error (RMSE) of calibration was obtained for LIBS data acquired at a laser wavelength of 532 nm and an excitation energy of 45 mJ. The PLS calibration models developed using multivariate analysis and subsequent cross validation confirmed that the best performance ( $r_{\text{cal}} = 0.97$  and  $\text{RMSE}_{\text{cal}} = 0.25$ ,  $r_{\text{val}} = 0.96$  and  $\text{RMSE}_{\text{val}} = 0.31$ ) was obtained in the same experimental conditions as those indicated above. Additional emission lines in the range

230–262 nm were identified as contributing significantly in building the calibration model. In particular, the Fe lines were correlated with the C peaks present in soil samples, thus justifying the covariance of Fe and C. In conclusion, the potential and convenience of a coupled LIBS-chemometric approach was successful in constructing a calibration model that could be used to quantify OC in soils with different contents of clay, silt and sand, i.e. independently of the soil series. A laser wavelength of 532 nm and excitation energy of 45 mJ were recommended to be used as experimental conditions in future studies aiming to expand and validate the model developed to confirm its robustness in measuring the C content in a broader range of soils.

An improved method aiming to avoid the interference of neutral and singly ionized Fe lines on the standard LIBS measurement of the atomic C I line at 247.8 nm was explored successfully by Glumac et al. [39]. The authors used a Nd:YAG laser operating at a wavelength of 532 nm and low power to find out an optimized combination of high dispersion and appropriate time gating strategy of the LIBS signal in order to minimize interference signals while maintaining a high signal-to-noise ratio. This approach would allow the accurate measurement of the C content in soil down to the subpercent level in the presence of Fe interferences. Six dried, pelletized sandy loam or silty loam soil samples containing OC in the range from 0.5 to 3% (w/w) were collected at depths of 0–25 cm from areas under various farming systems, and analysed for their C content by LIBS and a reference conventional thermal oxidation method. In order to develop an optimized detection strategy to analyse soil samples, a preliminary series of experiments was performed by evaluating the temporal evolution of the LIBS spectra of pelletized samples of control graphite and Fe oxide by varying the detection gate delay from 1 to 10  $\mu\text{s}$  with a constant gate width of 1  $\mu\text{s}$ . Each sample was tested by LIBS four times, twice on each side of the disk pellet, by using an average of 100 laser shots each, for a total of 400 shots per sample. The potential interference of the Fe II signal superimposed to the C I line was identified, quantified and minimized in soil samples by using appropriate gate timing parameters. Further, the high spectral resolution used allowed to differentiate clearly between the C I line and adjacent Fe I and Fe II lines. The LIBS C I signal at 247.8 nm, as measured at an average laser power of 35 mJ and a constant gate delay time of 3  $\mu\text{s}$  resulted highly correlated (coefficient of determination,  $r^2 = 0.94$ ) with the OC content measured by dry combustion. In conclusion, (i) despite minor limitations, the acceptable performance of the low laser energies used would represent a major system-design advantage for the development of low-power portable LIBS instruments for field application; (ii) although Fe-rich soils were not investigated, the promising results obtained suggested that the Fe correction factor could be applied with success to the analysis of soils with much greater Fe content; (iii) the use of robust multivariate analysis such as PCA or PLS for weak signals was not needed; and (iv) the use of element ratios, e.g. C/Si or C/(Al + Si), was not required to generate accurate measurements of soil C content. However, although the LIBS technique appears quite robust for laboratory analysis of dry soil samples, further work was suggested to evaluate the effects of soil moisture and density, and to develop further the LIBS technique in order to assess soil C in the field.

More recently, Ayyalasomayajula et al. [40] used a Q-switched Nd:YAG laser at the excitation wavelength of 532 nm provided with ICCD to evaluate the C content in six pellets obtained by mixing a finely ground and sieved soil sample from Mississippi and C powder at six different C concentrations ranging from 3.74 to 9.74%, including a blank (no C powder added to soil). Ten spectra were acquired from each sample, and each spectrum was an average of five shots. The pellets were analysed for their C content in triplicate both by LIBS, as mounted on a platform rotating at various speed in



order to shoot various areas of the sample, and by a CHN analyzer. To optimize the signal-to-noise ratio and reduce the relative standard deviation (RSD) values, the LIBS spectra (Fig. 4) were recorded using varying experimental conditions, including lens-to-sample distance, laser energy per pulse, gate delay and width, and sample rotation speed. Two models, i.e. simple linear regression (SLR) and multiple linear regression (MLR) [41,42], were used in developing the calibration curves and data validation. Due to their spectrograph limitation, the authors used the C I line at 247.8 nm and the ratios of total peak areas of the C I line and Fe lines at 246.51 nm and 247.48 nm to account for the Fe lines interference. Both calibration methods yielded excellent  $r^2$  values ( $>0.99$ ) and relative accuracy ( $RA > 5\%$ ), with uncertainty and  $RA\%$  values improved when using the MLR model (Fig. 5), especially for samples used in the validation.

### 3.2. Use of the C I emission line at 193 nm

The potential interference of the Fe line on the C line at 247.8 nm prompted Ebinger et al. [43] to investigate the performance of the strong 193-nm C line, which shows no interference from Fe, to evaluate the C content of the same soil samples by the same LIBS apparatus used by Cremers et al. [36]. The ratio of the C line intensity at 193 nm to the sum of the intensities of the ionic Al and neutral Si peaks (respectively at approximately 199 and 212 nm), which were assumed to remain constant in the samples, was plotted versus the soil OC concentration measured by dry combustion. The use of this line intensity ratio in the standardization procedure allowed to obtain an analytical signal more robust than that obtained when using the C line alone or the ratio of the C line to either Al or Si line. This result was ascribed to the reduced variations in emission line intensities due to differences in ablated material and excitation conditions. The calibration curve yielded an excellent  $r^2$  value ( $r^2 = 0.99$ ,  $p < 0.001$ ), and the verification plot confirmed the excellent relationship ( $r^2 = 0.95$ ,  $p < 0.001$ ) between LIBS data and dry combustion data for all soils tested, which also supported the assumption that Al and Si concentrations were almost constant among samples. Further, calibration curves obtained by repeating LIBS data collection each day for 30 consecutive days showed a good reproducibility (average  $r^2 = 0.97$ ) of the method for the soils examined. Thus, the use of the C line at 193 nm

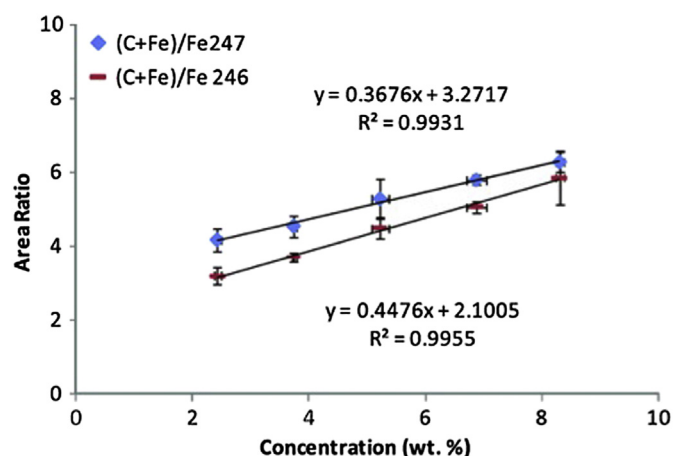


Fig. 5. Calibration plots based on line-intensity ratios of C using a modified SLR method. Reprinted from Applied Optics, Vol. 51, K.K. Ayyalasomayajula et al., Application of laser-induced breakdown spectroscopy for total carbon quantification in soil samples, pp B149–B154. Copyright 2012, with permission from Optical Society.

allowed to avoid the C–Fe interference without problems for C quantification due to the presence of the Al II line at 199 nm. However, additional tests, possibly using a field-portable LIBS instrument, would be required to evaluate a wider range of soils with different texture and mineralogy.

Some years later, da Silva et al. [44] were the first to attempt C quantification directly in whole tropical soil samples by using a calibrated portable Nd:YAG LIBS system in field conditions without any (or minimal) soil pre-treatment. Six Argisols from Brazilian Cerrado, each collected at six different depths (from 0 to 100 cm) to obtain a C content gradient, were analysed in the form of pellets by LIBS and dry combustion using a total organic carbon analyzer (TOC). To improve the signal-to-noise ratio sixty LIBS spectra were obtained each from one shot in different areas of each sample, and the final spectrum was averaged. To avoid the interference by Fe, of which tropical soils are very rich, the C line at 193 nm was preferred to the C line at 247.8 nm. Although the portable LIBS equipment used had a low resolution and a large number of emission lines were observed in the spectra due to the very heterogeneous soil

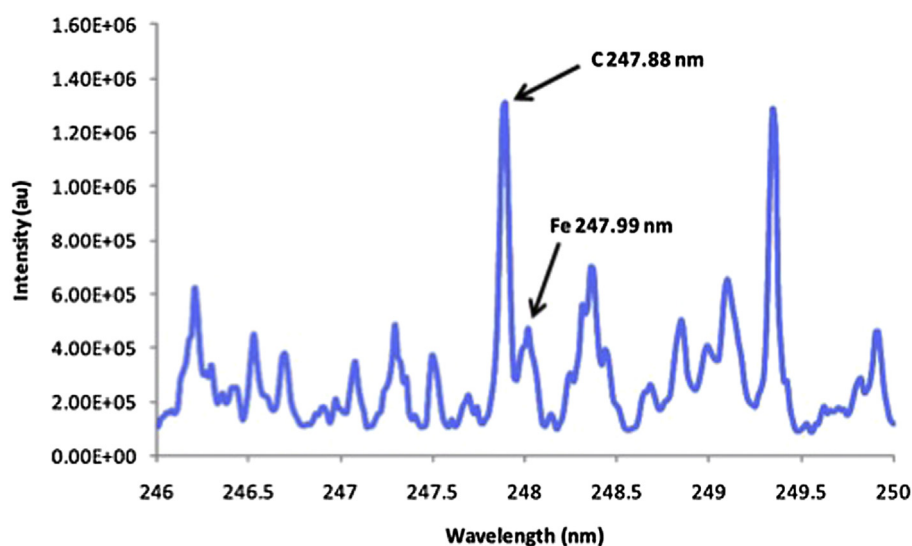


Fig. 4. Spectrum of emission lines selected for LIBS analysis. Reprinted from Applied Optics, Vol. 51, K.K. Ayyalasomayajula et al., Application of laser-induced breakdown spectroscopy for total carbon quantification in soil samples, pp B149–B154. Copyright 2012, with permission from Optical Society.

matrix, the latter effect could be minimized and the spectral baseline could be corrected by using a dedicate computer program. Thus, the C signal at about 193 nm could be clearly distinguished and measured, and good linear correlations (respectively  $r = 0.95$  for SRL and  $r = 0.97$  for MLR) were obtained by fitting LIBS-C versus TOC-C with no interference problems arising from the very close line of Al at 193.70 nm. Cross validation of data confirmed the accuracy of the method by providing a correlation coefficient of  $r = 0.91$ . In conclusion, the great potential of portable LIBS systems with low resolution was shown for quantitative C measurements *in situ* in tropical soils.

### 3.3. Comparison between the C I emission lines at 247.8 and 193 nm

The important limitation of portable LIBS systems for soil C analysis *in situ*, i.e. the spectral resolution/separation of the Al lines interference from the C emission line, prompted Nicolodelli et al. [45] to develop and test a method aiming to solve this drawback. Fifty three samples were collected from the various horizons of two forest soil profiles typical of Brazil, a spodosol from the Amazon region and an oxisols from the Atlantic coast, and analysed by a Q-switched Nd:YAG laser at the wavelength of 1064 nm. To improve the signal-to-noise ratio sixty LIBS spectra in the range from 189 to 966 nm, each measured after two laser shots, were acquired for each soil sample, and then averaged. A mathematical method, i.e. the spectral angle mapper (SAM), was applied to remove outlier spectra that did not show a behavior similar to the majority of them. The performance of the two more studied LIBS C lines at 193 and 247.8 nm were evaluated comparatively to the soil C content measured by a CHNS/O elemental analyzer. No Fe lines interfering with the C line at 247.8 nm were detected in the LIBS spectra of spodosol samples, possibly due to the Fe concentration below the LIBS limit of detection, whereas the spectra of oxisols showed serious interferences by Fe, Ti and Si lines, especially by the Fe line at 247.94. Differently, the C line at 193 nm was clearly overlapped by the three Al lines at 193.04, 193.16 and 193.58 nm, which could not be resolved spectrally by the portable low-resolution LIBS apparatus used in this work. The novel correction method tested was able to remove the Al interference with the C line at 193 nm using the C line at 247.8 nm as reference. Further, the calibration curves obtained by fitting in a logarithmic scale model the intensity of the corrected C line at 193 nm and C data from elemental analysis showed correlation coefficients of  $r = 0.97$  for spodosols and  $r = 0.91$  for oxisols. Cross validation of data yielded a correlation coefficient of  $r = 0.91$  and a mean error of about 19%. Thus, the good results obtained support the validity of the proposed method for correcting the Al interference on the C I LIBS emission line at 193 nm, and confirm the potential of LIBS for *in situ* quantitative analysis of C using a portable, low-resolution LIBS apparatus.

Very recently, Nguyen et al. [46] evaluated comparatively the efficiency of the two LIBS C I wavelengths at 193 and 247.8 nm to measure C concentrations on pellets of three Korean soils of different chemical and physical properties collected from a wetland, a forest and a sediment area, using five reference soil samples of certified C concentration for LIBS spectra calibration. A Nd-YAG laser apparatus operating at a wavelength of 532 nm and energy of 30.5 mJ was used to obtain forty LIBS spectra by shooting two times on twenty spots of two pellets for each sample, with a first shot applied to clean the sample surface. To enhance the accuracy of LIBS measurements, the effects of some crucial experimental parameters, including focal length lenses, laser energy per pulse and delay times, on the signal-to-noise ratio and RSD were tested. When considering the C I line at 247.8 nm, a delay time of 1.4  $\mu$ s was found to be the best value to maximize the C I line intensity

and minimize the intensities of the Fe overlapping peak at 247.8 nm and of the adjacent Fe peaks at 247.97 and 248.28 nm. The calibration curve developed by SLR showed a very good correlation ( $r = 0.994$ ) between the ratio of the areas of the C I peak at 247.8 nm to the Fe peak at 248.28 nm measured at a delay time of 1.4  $\mu$ s and the C% of reference soils. As well, the verification test provided a very good correlation ( $r = 0.992$ ) between the C content measured by LIBS and certified values. The RA% was better for samples with higher C/Fe ratio. For the C I line at 193 nm no significant difference was apparent among the LIBS spectra obtained using various delay times, thus the authors applied the same delay time used above, i.e. 1.4  $\mu$ s (Fig. 6). A very good correlation ( $r = 0.998$ ) was shown by the calibration curve developed by correlating the ratio of the peak intensity of the C I line at 193 nm and the sum of the intensities of Al and Si lines, respectively at 198.90 and 212.40 nm, and the C % certified values (Fig. 7a). Further, the verification plot showed an excellent correlation ( $r = 0.997$ ) between the C content predicted by LIBS and certified values (Fig. 7b). In conclusion, although both C I lines examined provided very significant linear correlations and high RA% in predicting the C concentrations in unknown soil samples, the use of the C I line at 193 nm yielded more accurate results for soils with low C content. Although the C/(Al + Si) peak intensity ratio was found to be more consistent than the C peak intensity alone, and was used successfully for the sandy and sandy loam soils examined, the contents of Al to Si can vary largely among soils, thus further studies should be carried out for soils with larger differences in chemical and textural features. Future studies should also reconsider the possible use of the C I line at 247.8 nm by minimizing further the Fe interference on it, e.g. by using a high dispersion LIBS instrument of modest focal length and an ICCD camera.

### 3.4. Use of other C emission lines at high wavelengths

Belkov et al. [47] explored comparatively the potential use of C lines at wavelengths much higher than those discussed above to measure soil C content. A Q-switched Nd-YAG laser system operating at 1064 nm was used in two different modes for ablating, exciting and recording LIBS emission spectra of two sets of topsoil samples collected at various depth. In the range 810–910 nm the

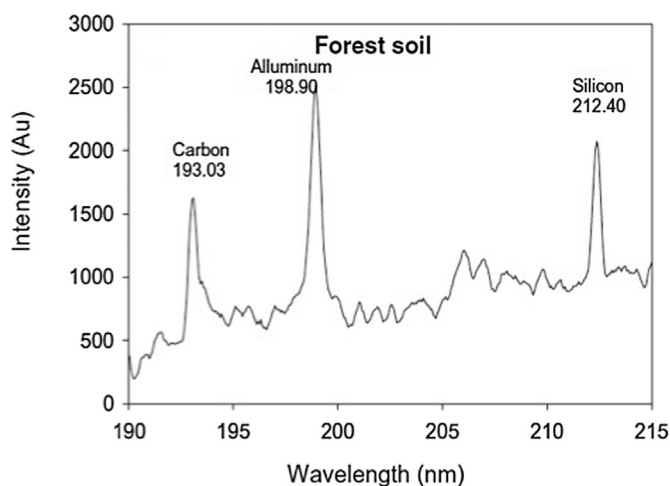
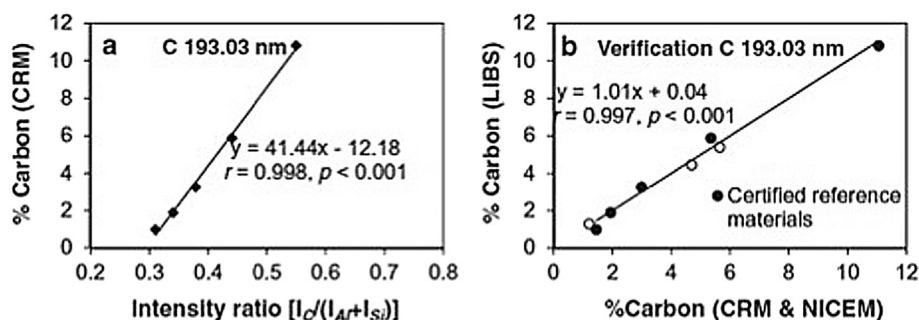


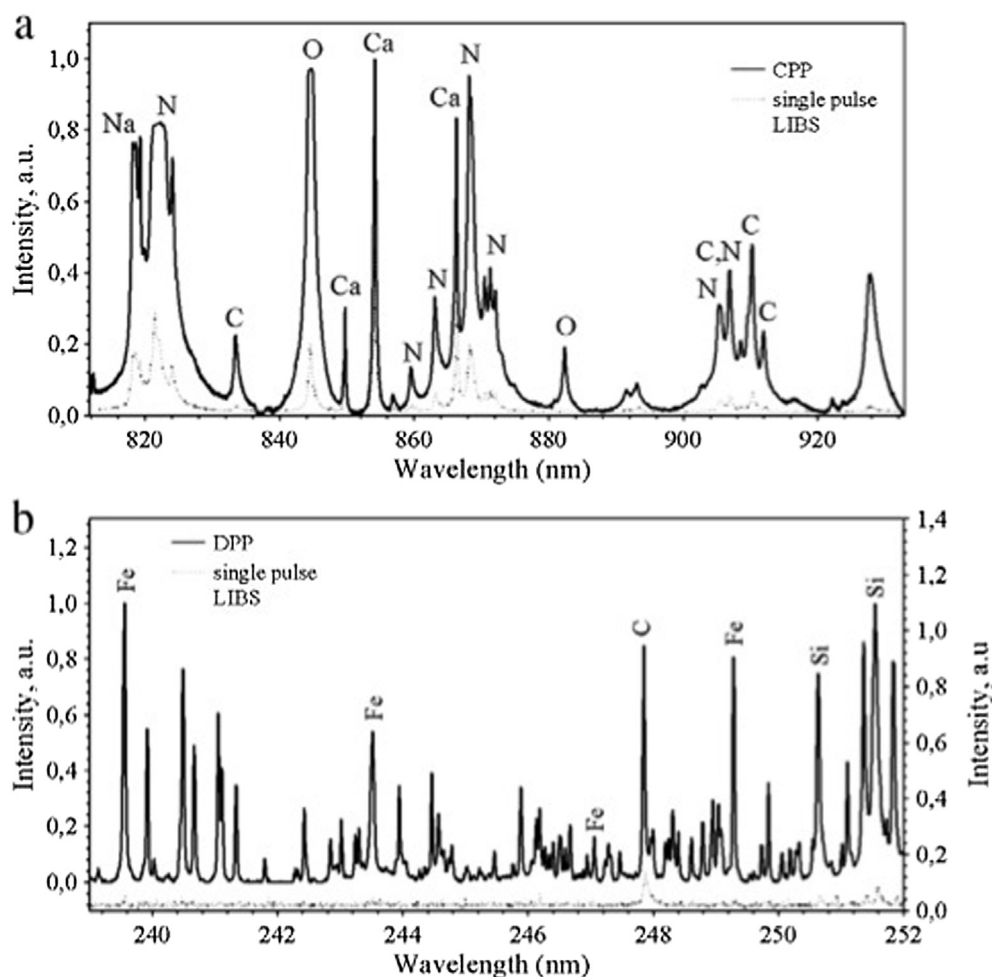
Fig. 6. LIBS spectrum in the region from 190 to 215 nm measured on a forest soil sample at a delay time of 1.4  $\mu$ s. Reprinted from Environ. Monit. Assess. Vol. 187, H.V.-M. Nguyen et al., Improving the application of laser-induced breakdown spectroscopy for the determination of total carbon in soils, pp 28. Copyright 2015, with permission from Springer.



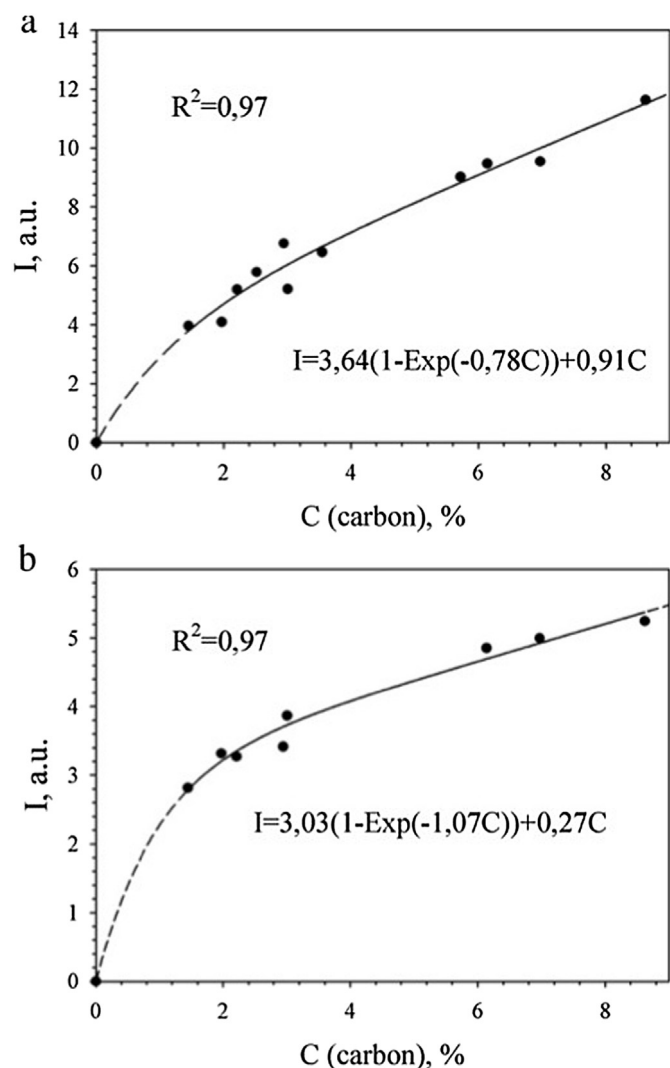
**Fig. 7.** Calibration (a) and verification (b) plots based on the line-intensity ratio of C at 193.03 nm. The verification was performed using LIBS data from certified reference materials and unknown samples. Reprinted from *Environ. Monit. Assess.* Vol. 187, H.V.-M. Nguyen et al., Improving the application of laser-induced breakdown spectroscopy for the determination of total carbon in soils, pp 28. Copyright 2015, with permission from Springer.

combined (single) pulse plasma (CPP) mode was used at a pulse energy of 180 mJ with a CCD array. LIBS signal intensities increased due to the synchronous action obtained by superposing a spark excitation of the plasma plume on the laser ablation plume produced by a focused laser beam on the sample surface [48–50]. In the range 239–340 nm the more conventional double pulse plasma (DPP) laser mode was used at 50 mJ pulse energy by focusing ten double shots on the sample surface. This application provided a more efficient production of analyte species in the excited state and

increased the signal-to-noise ratio [51–53]. With respect to CPP, the DPP mode enhanced by a factor of 7 the intensity of the C I line at 247.8 nm, whereas the intensity of the C I line at 833.52 nm was enhanced 20 times in the CPP mode (Fig. 8). The plots of C I line intensities obtained by either the DPP or the CPP mode versus the soil C content measured by elemental analysis showed a non linear trend with a good  $r^2$  value (0.97) (Fig. 9). A group of intense C lines observed in the IR range of CPP emission, with the most intense at 909.48 nm, could not be resolved completely due to the



**Fig. 8.** CPP single-pulse (a) and DPP single-pulse (b) LIBS spectra (C = 3.55%). Reprinted from *Spectrochimica Acta B*, Vol. 64, M.V. Belkov et al., Comparison of two laser-induced breakdown spectroscopy techniques for total carbon measurement in soils, pp 899–904. Copyright 2009, with permission from Elsevier.



**Fig. 9.** Calibrations graphs for CPP mode (a) DPP mode (b). Reprinted from *Spectrochimica Acta B*, Vol. 64, M.V. Belkov et al., Comparison of two laser-induced breakdown spectroscopy techniques for total carbon measurement in soils, pp 899–904. Copyright 2009, with permission from Elsevier.

interference effect by air N lines. In an attempt to resolve these lines by applying an appropriate procedure, a calibration graph was produced which resembled the one obtained for the C I line at 833.52 nm, but having a lower  $r^2$  value (0.82).

In conclusion, the DPP mode allowed to record LIBS spectral emissions of C and other relevant elements present in soil in the visible and UV ranges, whereas the red visible and IR ranges performed best in the CPP mode. Further, the CPP mode implied several advantages over the DPP mode, which include: line intensity amplification, due to the increase of plasma volume and duration of plasma emission; higher concentration sensitivity; smaller influence of laser pulse energy instability on line intensity; and the possible use of low-cost, portable LIBS instrumentation.

### 3.5. Differentiation between total C, inorganic C and organic C by LIBS

Bricklemeyer et al. [54] were the first to attempt to distinguish between total C (TC), inorganic C (IC) and organic C (OC) in field-moist, intact soil cores without any soil physical pretreatment by

the use of LIBS in the spectral range from 200 to 300 nm, in comparison to standard dry combustion (for TC) and calcimetric (for IC) methods. The analyses were conducted in the laboratory on a set of 306 samples from 78 intact, field-moist, 50-cm-deep soil cores collected from north-central Montana. The classical PLS1 model and its similar but more advanced PLS2 model were both used to calibrate LIBS data selected randomly from 58 cores representing 227 samples, whereas the validation was performed on data from the remaining 79 samples from the other 20 soil cores. The calibration and cross-validation performed by PLS2 were worse than those obtained by PLS1. However, the independent validation performed by PLS2 resulted more stable and robust than that obtained by PLS1 for TC, IC and OC measurements, which yielded predictions with coefficients of determinations of  $r^2 = 0.66$  for IC,  $r^2 = 0.63$  for TC, and  $r^2 = 0.22$  for OC. Thus, only semiquantitative validation accuracies could be achieved for TC and IC, whereas the capability of LIBS to predict OC was very low possibly due to the low OC variance of the soils used and other factors, including the limited low spectral range used in this work, which could not capture emissions from several other elements associated with OC. The strong correlation shown between conventionally-measured TC and IC for the soils studied raised questions regarding the potential of LIBS-PLS models to even distinguish TC and IC. However, the stoichiometric relationships between C and elements related to C in the soil matrix utilized in the calibration, as suggested by the regression coefficients from the PLS2 model, would support the chemometric separation between TC and IC. Besides the major C emission at 247.8 nm, other emissions, including those of Si, Mg and Ca, were found to be important predictors for TC and IC, whereas regression coefficients for OC were all close to zero as expected by the weak calibration. In conclusion, when compared to LIBS data obtained on dry, powdered and pelletized samples, the acquisition of high-quality LIBS data from undisturbed soil core surfaces presents a number of drawbacks, including the presence of moisture, plant litters, roots and uneven sample surfaces, and low sample density.

The unsatisfactory results obtained in their first work prompted Bricklemeyer et al. [55] to attempt the use of a complete LIBS spectrum (245–925 nm) and two approaches more advanced than the PLS2 model, i.e. LASSO and MRCE, for identifying the more important elemental predictors able to improve the calibration and prediction accuracy in the direct measurement of soil TC, IC and OC. Differently from PLS models, which use all available spectral channels as predictors, including also not useful ones that may contribute to prediction errors, LASSO and MRCE reduce the number of predictor variables in the regression model by retaining only meaningful single channels or small spectral regions as predictors. Sixty intact 50-cm-deep soil cores were collected from Mollisols, Entisols and Inceptisols from six wheat fields in north-central Montana. The cores were then analysed in the laboratory on nine points at each of eight soil depths, thus providing seventy two LIBS spectra per core for a total of 4320 spectra. Some matrix drawbacks shown to reduce the calibration prediction accuracy in the authors' previous work [54] were addressed by increasing: (i) the laser focal length from 50 to 500 mm, in order to reduce the changes in distance due to the sample surface roughness and fractures; and (ii) the laser energy from 80 to 100 mJ per pulse to account for the energy lost for soil moisture vaporization. With respect to the PLS2 model, the LASSO and MRCE calibrations achieved improved quantitative accuracy for TC ( $r^2 = 0.89$  and  $r^2 = 0.80$ , respectively) and IC ( $r^2 = 0.85$  and  $r^2 = 0.91$ , respectively), and semi-quantitative accuracy for OC ( $r^2 = 0.63$  and  $r^2 = 0.54$ , respectively). The cross-validation performance maintained the quantitative accuracy of the corresponding calibration for predicting IC, but the accuracy decreased to semi-quantitative

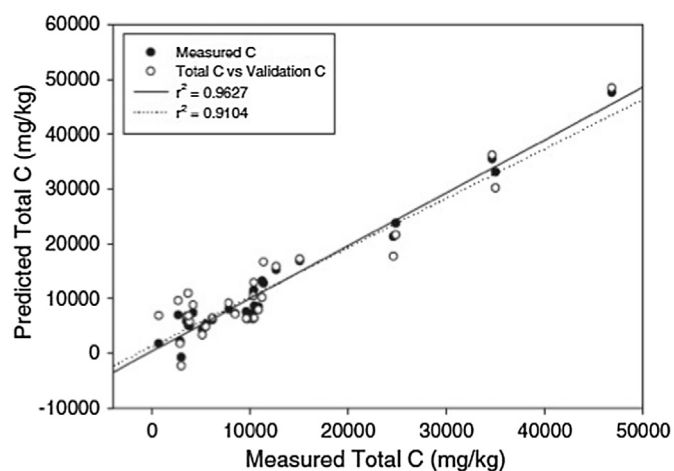


for TC and failed for OC. The complexity of soil OC, which includes plant residues and microbial biomass present in soil, and the low OC range of soils examined (from 1.85 to 2.17%) may have contributed to the poor chemometric model performance for OC. The regression coefficients of the whole spectrum indicated that, besides C, several lines of the elements Fe, Mg, Ca, Na, Si, K and S were used as important predictors by the models for determining IC, OC and TC. This suggested the existence of complex and diverse stoichiometric biogeochemical correlations and chemical matrix effects that could not be interpreted easily. Additional research by innovative approaches is thus needed to improve the performance of chemometric models and their prediction accuracies, especially for the soil OC fraction, and additional testing with increased soil diversity is required to extend the application of LIBS to *in situ* soil analyses.

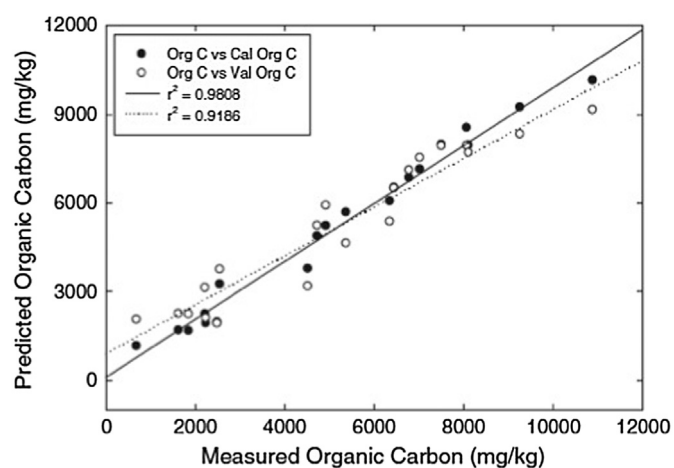
Simultaneously to Bricklemeyer et al. [55], Martin et al. [56] explored a different strategy to differentiate between TC, IC and OC by acquiring LIBS spectra over a wide wavelength range, i.e. 200–800 nm, which contained systematic and consistent spectral signatures of all elements that occurred in each soil sample. A Q-switched Nd:YAG laser with output wavelength of 532 nm and laser power of 45 mJ was used to analyse a set of fifty eight soil samples having a dominant content of either IC or OC. Soil samples were collected from various horizons of five soil orders, including nine Ultisols, eleven Alfisols, thirty three Mollisols, four Vertisols and one Spodosol, and then analysed on the sieved <2-mm fraction obtained after air- or oven-drying at 60 °C and grinding. The full spectral LIBS data were analysed by two multivariate chemometric methods different from those used by Bricklemeyer et al. [55], i.e. PCA and PLS. Half of the spectra were used to construct the calibration model and the remaining half to validate the calibration. Both models yielded similar and very good results for TC, IC and OC concentrations in all soils examined. The  $r^2$  values for the calibration and validation curves were, respectively,  $r^2 = 0.96$  and  $r^2 = 0.91$  for TC (Fig. 10),  $r^2 = 0.94$  and  $r^2 = 0.87$  for IC, and  $r^2 = 0.98$  and  $r^2 = 0.91$  for OC (Fig. 11). The RMSE values for the calibration and validation were, respectively, 4.1% and 7.5% for TC, 5.4% and 8.3% for IC and 3.9% and 8.4% for OC. The relatively high RMSE values were reasonably expected due to the heterogeneity of soils analysed that belong to different orders with different chemical and physical properties. The loading parameters that contributed most to the correlation of TC and IC to soil chemical composition were identified as the peaks of Ti, Si, Al, Fe and Ca. This result suggested the existence of a stoichiometric relationship between TC and IC and these typical mineral constituent elements in the soil matrix. Differently, the prominent loading parameter correlated to OC was only the peak of Mg, whereas all other elements contributed to a lesser extent to determine the OC concentration. Thus, the intensity ratio of the  $Mg^{+2}$  line at 279.7 nm to the  $Ca^{+2}$  line at 397 nm was proposed to differentiate IC-rich versus OC-rich soils, and a value of 0.263 for OC-rich soils and 0.148 for IC-rich soils were calculated. Although the viability of the LIBS technique associated with PCA and PLS was elegantly demonstrated to be able to differentiate OC versus IC in a wide range of soils, more work is needed to: (i) extend the application of LIBS to soils of different nature and origin; (ii) confirm the correlation of TC and IC with rock-forming elements and OC with Mg; and (iii) support the diagnostic values of the Ca/Mg ratio to differentiate soils containing predominantly OC or IC.

### 3.6. Comparison of LIBS to DRIFTS and INS techniques for soil C measurement in the field

The performance of a portable LIBS system in measuring soil C density in the field on a number of soil samples in two different

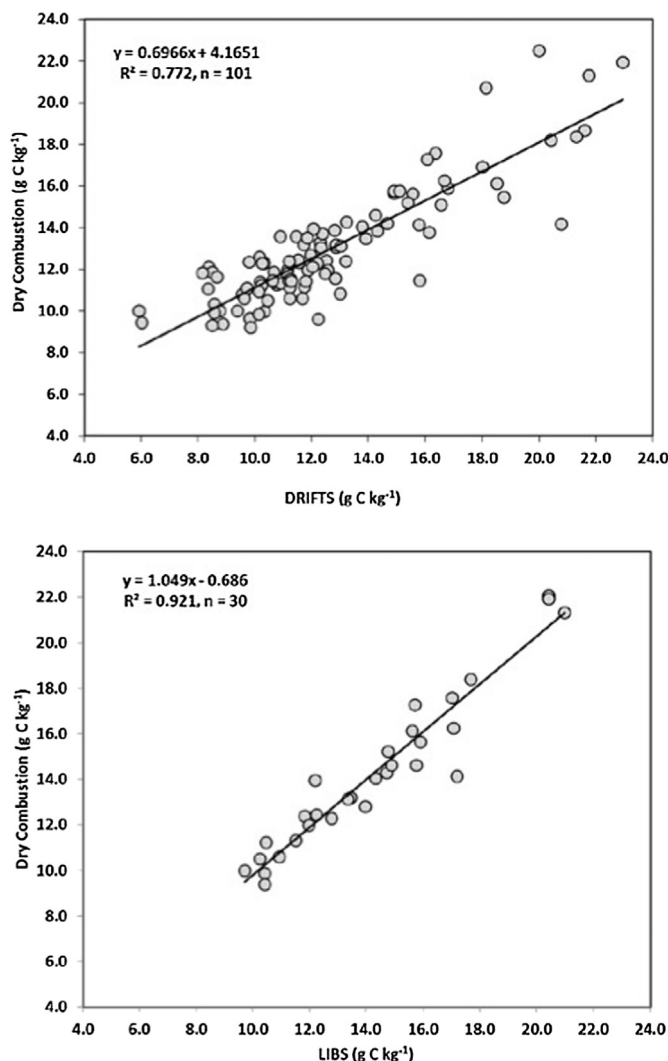


**Fig. 10.** A multivariate model showing the correlation between conventionally measured C content and total C content predicted by LIBS. The solid and dotted lines represent the samples included in the calibration and validation sets, respectively. Reprinted from Spectrochimica Acta B, Vol. 87, M.Z. Martin et al., Investigation of laser-induced breakdown spectroscopy and multivariate analysis for differentiating inorganic and organic C in a variety of soils, pp 100–107. Copyright 2013, with permission from Elsevier.



**Fig. 11.** A multivariate model showing the correlation between conventionally measured C content and organic C content predicted by LIBS. The solid and dotted lines represent the samples included in the calibration and validation sets, respectively. Reprinted from Spectrochimica Acta B, Vol. 87, M.Z. Martin et al., Investigation of laser-induced breakdown spectroscopy and multivariate analysis for differentiating inorganic and organic C in a variety of soils, pp 100–107. Copyright 2013, with permission from Elsevier.

sites at depths of 0–30 cm was evaluated in comparison to that obtained using two other advanced techniques, i.e. DRIFTS and INS, and the traditional laboratory dry combustion method [57]. Although the three portable instruments showed acceptable performances under field conditions, they required improvement in terms of calibration. As a whole, dry combustion data for soil C density were much better correlated with LIBS data (coefficient of determination,  $r^2 = 0.921$ ) than with DRIFTS data (coefficient of determination,  $r^2 = 0.772$ ) (Fig. 12). However, the LIBS and DRIFTS techniques required soil sampling and soil bulk density information to convert soil C concentrations into soil C density, whereas INS required only some soil sampling for establishing correlations between INS data and dry combustion data, but no further sampling once these were established.



**Fig. 12.** Comparison of calibration lines obtained by DRIFTS (a) and LIBS (b) including 10% of the data in the calibration sets. Reprinted from PLoS ONE, Vol. 8 (1), R.C. Izaurralde et al., Evaluation of three field-based methods for quantifying soil carbon, e55560. Copyright 2013, with permission from PLoS ONE.

#### 4. Brief summary of advantages and limitations of LIBS for the measurement of soil C content, including some final remarks and future perspectives

The emerging application of the LIBS technique to measure quantitatively soil C, and especially soil organic C, shows appeal on the basis of the promising results obtained up-to-day as summarized above. The sensitivity, selectivity, accuracy and precision of LIBS appear comparable to those of traditional dry combustion/elemental analysis techniques. Specific advantages that make LIBS an attractive powerful analytical tool alternative to traditional methods are: the requirement of no (or minimum) sample preparation thus minimizing soil disturbance, its relative simplicity, short analytical time of the order of minutes, and the possibility to analyse a huge number of samples daily, with related cost efficiency. An important added value of LIBS is the potential application of miniaturized field-portable instrumentation with precision and accuracy close to those of laboratory instruments, which can be used directly *in situ* for a reliable, rapid, repetitive and sequential measurement of C in a large number of surface and core soil samples from intact profiles at various depths in large areas in a variety

of locations at spatially and temporally meaningful scales and relatively low cost.

However, a number of limitations and drawbacks still exist and need to be solved to strengthen the application of LIBS to soil C quantification, especially in the field. Instrumental LIBS drawbacks include: the control of ablation and plasma formation, evolution and interaction with the surrounding environment, the achievement of equilibrium conditions in the plasma, and the elimination of self-absorption effects that may result in reduction of signal intensity for elements at high concentrations, thus making their quantification difficult or even impossible. Further, a number of soil physical and chemical properties, including structure, mineralogy, morphology, inorganic C (carbonates) content, moisture, may introduce uncertainties in the LIBS measurement of soil organic C due to the effects of soil matrix in which organic C is embedded. In particular, factors contributing to matrix effects include: changes in the ablated amount of the various elements due to differences in heat capacity and vaporization temperatures and variations in element ionization in the plasma. Currently, calibration and validation curves of soil C measured by dry combustion/elemental analysis methods versus LIBS peak intensity/area have been developed using various methods with various success, however a single and robust calibration model that results reproducible for a broad range of soil types still needs to be developed. Further, field application of LIBS will require instruments ensuring ruggedness, stability and reliability, and calibration models tested for a variety of soil matrices. Thus, a number of instrumental, methodological and procedural challenges must be faced, and possibly solved, in future research with the ultimate goal of producing soil-specific databases to be used universally for a robust soil C analysis by LIBS.

#### References

- [1] Climate Change, The Scientific Basis, (Intergovernmental Panel Climate Change, 2001, 2001 available in, [http://www.grida.no/climate/ipcc\\_tar/wg1/index.htm](http://www.grida.no/climate/ipcc_tar/wg1/index.htm), at October, 26th 2007.
- [2] N. Senesi, E. Loffredo, The chemistry of soil organic matter, in: D.L. Sparks (Ed.), *Soil Physical Chemistry*, CRC Press, Boca Raton, 1999, pp. 239–370.
- [3] D.J. Greenland, Carbon sequestration in soil: knowledge gaps indicated by the symposium presentations, in: R. Lal, J.M. Kimble, R.F. Follett, B.A. Stewart (Eds.), *Soil Processes and the Carbon Cycle*, CRC Press, Boca Raton, 1998, pp. 591–594.
- [4] Department of Energy (DOE), Carbon Sequestration Research and Development, DOE Report DOE/SC/FE-1, Washington, DC, 1999. Available on-line at: [http://www.ornl.gov/carbon\\_sequestration](http://www.ornl.gov/carbon_sequestration).
- [5] P. Falkowski, R.J. Scholes, E. Boyle, J. Canadell, D. Canfield, J. Elser, N. Gruber, K. Hibbard, P. Hogberg, S. Linder, F.T. Mackenzie, B. Moore III, T. Pedersen, Y. Rosenthal, S. Seitzinger, V. Smetacek, W. Steffen, The global carbon cycle: a test of our knowledge of earth as a system, *Science* 290 (2000) 291–296.
- [6] R.J. Scholes, I.R. Noble, Climate change: storing carbon on land, *Science* 294 (2001) 1012–1013.
- [7] D.D. Breshears, C.D. Allen, The importance of rapid disturbance-induced losses in carbon management and sequestration, *Glob. Ecol. Biogeogr.* 11 (2002) 1–5.
- [8] A. Walkley, An examination of methods for determining organic C and nitrogen in soils, *J. Agr. Sci.* 25 (1935) 598–609.
- [9] D.W. Nelson, L.E. Sommers, Total carbon, organic carbon, organic matter, in: D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert (Eds.), *Methods of Soil Analysis. Part 3—Chemical Methods*, SSSA and ASA, Madison, 1996, pp. 961–1010.
- [10] J.M. Kimble, R. Lal, R.F. Follett, Methods for assessing soil C pools, in: J.M. Kimble, R.F. Follett, B.A. Stewart (Eds.), *Assessment Methods for Soil Carbon*, Lewis Publ., Boca Raton, 2001, pp. 3–12.
- [11] G.W. McCarty, J.B. Reeves III, Development of rapid instrumental methods for measuring soil organic carbon, in: J.M. Kimble, R.F. Follett, B.A. Stewart (Eds.), *Assessment Methods for Soil Carbon*, Lewis Publ., Boca Raton, 2001, pp. 371–380.
- [12] L. Wielopolski, I. Orion, G. Hendrey, H. Rogers, Soil carbon measurements using inelastic neutron scattering, *IEEE Trans. Nucl. Sci.* 47 (2000) 914–917.
- [13] L. Wielopolski, S. Mitra, G. Hendrey, H. Rogers, A. Torbert, S. Prior, Non-destructive *in situ* soil carbon analysis: principles and results, in: *Proc. 2nd Nat. Conf. Carbon Sequestration: Developing and Validating the Technology Base to Reduce Carbon Intensity*, 5–8 May, 2003 (Alexandria, VA).
- [14] G.W. McCarty, J.B. Reeves III, V.B. Reeves, R.F. Follett, J.M. Kimble, Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon

- measurement, *Soil Sci. Soc. Am. J.* 66 (2002) 640–646.
- [15] F. Chen, D.E. Kissel, L.T. West, W. Adkins, Field-scale mapping of surface soil organic carbon using remotely sensed imagery, *Soil Sci. Soc. Am. J.* 64 (2000) 746–753.
  - [16] R.J. Gehl, C.W. Rice, Emerging technologies for *in situ* measurement of soil carbon, *Clim. Chang.* 80 (2007) 43–54, <http://dx.doi.org/10.1007/s10584-006-9150-2>.
  - [17] R.N. Fernandez, D.G. Schulze, D.L. Coffin, G.E. Van Scoyoc, Color, organic matter, pesticide adsorption relationships in a soil landscape, *Soil Sci. Soc. Am. J.* 52 (1988) 1023–1026.
  - [18] D.A. Cremers, L.J. Radziemski, *Handbook of Laser-induced Breakdown Spectroscopy*, Wiley & Sons Ltd., Chichester, 2006.
  - [19] R.S. Harmon, R.E. Russo, Laser-induced breakdown spectroscopy, in: H.D. Holland, K.K. Turekian (Eds.), *Treatise on Geochemistry*, Elsevier Inc., New York, 2013, pp. 245–272.
  - [20] R.E. Russo, X. Mao, J.J. Gonzalez, V. Zorba, J. Yoo, Laser ablation in analytical chemistry, *Anal. Chem.* 85 (2013) 6162–6177.
  - [21] J.A.M. Van der Mullen, Excitation equilibria in plasmas: a classification, *Phys. Rep.* 2 (1990) 109–120.
  - [22] D.W. Hahn, N. Omenetto, Laser-induced breakdown spectroscopy (LIBS), part I: review of basic diagnostics and plasma–particle interactions: still-challenging issues within the analytical plasma community, *Appl. Spectrosc.* 64 (2010) 335A–366A.
  - [23] J. Bubltz, C. Dolle, W. Schade, A. Hartmann, R. Horn, Laser-induced Breakdown spectroscopy for soil diagnostics, *Eur. J. Soil Sci.* 52/2 (2001) 305–312.
  - [24] F. Capitelli, F. Colao, M.R. Provenzano, R. Fantoni, G. Brunetti, N. Senesi, Determination of heavy metals in soils by laser induced breakdown spectroscopy, *Geoderma* 106 (2002) 45–62.
  - [25] G.S. Senesi, M. Dell'Aglio, R. Gaudiuso, A. De Giacomo, C. Zaccane, O. De Pascale, T.M. Miano, M. Capitelli, Heavy metal concentrations in soils as determined by laser-induced breakdown spectroscopy (LIBS), with special emphasis on chromium, *Env. Res.* 109 (2009) 413–420.
  - [26] M. Dell'Aglio, R. Gaudiuso, G.S. Senesi, A. De Giacomo, C. Zaccane, T.M. Miano, O. De Pascale, Monitoring of Cr, Cu, Pb, V and Zn in polluted soils by laser induced breakdown spectroscopy (LIBS), *J. Environ. Monit.* 13 (2011) 1422–1426.
  - [27] E.C. Ferreira, E.J. Ferreira, P.R. Villas-Boas, G.S. Senesi, C.M. Carvalho, R.A. Romano, L. Martin-Neto, D.M.B.P. Milori, Novel estimation of the humification degree of soil organic matter by laser-induced breakdown spectroscopy (LIBS), *Spectrochim. Acta B* 99 (2014) 76–81.
  - [28] J.B. Sirven, B. Bousquet, L. Canioni, L. Sarger, Laser-induced breakdown spectroscopy of composite samples: comparison of advanced chemometrics methods, *Anal. Chem.* 78 (2006) 1462–1469.
  - [29] H. Martens, T. Naes, *Multivariate Calibration: a User-friendly Guide to Multivariate Calibration and Classification*, John Wiley & Sons, New York, 1989.
  - [30] S. Wold, M. Sjostrom, L. Eriksson, PLS-regression: a basic tool of chemometrics, *Chemom. Intell. Lab. Syst. Syst.* 58 (2001) 109–130.
  - [31] T. Naes, T. Isaksson, T. Fearn, T. Davies, *A User-friendly Guide to Multivariate Calibration and Classification*, NIR Publ., Chichester, 2002.
  - [32] S.M. Clegg, E. Sklute, M.D. Dyar, J.E. Barefield, R.C. Wiens, Multivariate analysis of remote laser-induced breakdown spectroscopy spectra using partial least squares, principal component analysis, and related techniques, *Spectrochim. Acta B* 64 (2009) 79–88.
  - [33] D.L. Death, A.P. Cunningham, L.J. Pollard, Multi-element and mineralogical analysis of mineral ores using laser induced breakdown spectroscopy and chemometric analysis, *Spectrochim. Acta B* 64 (2009) 1048–1058.
  - [34] R. Tibshirani, Regression shrinkage and selection via the Lasso, *J. Roy. Stat. Soc. B* 58 (1996) 267–288.
  - [35] A.J. Rothman, E. Levina, J. Zhu, Sparse multivariate regression with covariance estimation, *J. Comput. Graph. Stat.* 19 (2010) 947–962.
  - [36] D.A. Cremers, M.H. Ebinger, D.D. Breshears, P.J. Unkefer, S.A. Kammerdiener, M.J. Ferris, K.M. Catlett, J.R. Brown, Measuring total soil carbon with laser-induced breakdown spectroscopy (LIBS), *J. Environ. Qual.* 30 (2001) 2202–2206.
  - [37] M.Z. Martin, S.D. Wullschlegel, C.T. Garten Jr., A.V. Palumbo, Laser-induced breakdown spectroscopy for the environmental determination of total carbon and nitrogen in soils, *Appl. Opt.* 42 (2003) 2072–2077.
  - [38] M.Z. Martin, N. Labbé, N. André, S.D. Wullschlegel, R.D. Harris, M.H. Ebinger, Novel multivariate analysis for soil carbon measurements using Laser-Induced Breakdown Spectroscopy, *Soil Sci. Soc. Am. J.* 74 (2010) 87–93, <http://dx.doi.org/10.2136/sssaj2009.0102>.
  - [39] N.G. Glumac, W.K. Dong, W.M. Jarrell, Quantitative analysis of soil organic carbon using laser-induced breakdown spectroscopy: an improved method, *Soil Sci. Soc. Am. J.* 74 (2010) 1922–1928.
  - [40] K.K. Ayyalasomayajula, F. Yu-Yueh, J.P. Singh, D.L. McIntyre, J. Jain, Application of laser-induced breakdown spectroscopy for total carbon quantification in soil samples, *Appl. Opt.* 51 (2012) B149–B154.
  - [41] K.H. Esbensen, *Multivariate Data Analysis - in Practice*, fifth ed., Camo Software, Oslo, 2004.
  - [42] S. Weisberg, *Applied Linear Regression*, John Wiley & Sons, New York, 2005.
  - [43] M.H. Ebinger, M.L. Norfleet, D.D. Breshears, D.A. Cremers, M.J. Ferris, P.J. Unkefer, M.S. Lamb, K.L. Goddard, C.W. Meyer, Extending the applicability of laser-induced breakdown spectroscopy for total soil carbon measurement, *Soil Sci. Soc. Am. J.* 67 (2003) 1616–1619.
  - [44] R.M. Da Silva, D.M.B.P. Milori, E.C. Ferreira, E.J. Ferreira, F.J. Krug, L. Martin-Neto, Total carbon measurement in whole tropical soil sample, *Spectrochim. Acta B* 63 (2008) 1221–1224, <http://dx.doi.org/10.1016/j.sab.2008.09.003>.
  - [45] G. Nicolodelli, B.S. Marangoni, J.S. Cabral, P.R. Villas-Boas, G.S. Senesi, C.H. Dos Santos, R.A. Romano, A. Segnini, Y. Lucas, C.R. Montes, D.M.B.P. Milori, Quantification of total carbon in soil using laser-induced breakdown spectroscopy: a method to correct interference lines, *Appl. Opt.* 53 (2014) 2170–2176, <http://dx.doi.org/10.1364/AO.53.002170>.
  - [46] H.V.-M. Nguyen, S.-J. Moon, J.H. Choi, Improving the application of laser-induced breakdown spectroscopy for the determination of total carbon in soils, *Environ. Monit. Assess.* 187 (2015) 28, <http://dx.doi.org/10.1007/s10661-015-4286-z>.
  - [47] M.V. Belkov, V.S. Burakov, A. De Giacomo, V.V. Kiris, S.N. Raikov, N.V. Tarasenko, Comparison of two laser-induced breakdown spectroscopy techniques for total carbon measurement in soils, *Spectrochim. Acta B* 64 (2009) 899–904, <http://dx.doi.org/10.1016/j.sab.2009.07.019>.
  - [48] K. Laqua, *Analytical spectroscopy using laser atomizers*, in: N. Omenetto (Ed.), *Analytical Laser Spectroscopy*, Wiley, New York, 1979, pp. 159–182.
  - [49] O. Ayed Nassef, E.-A. Hanie, Spark discharge assisted laser induced breakdown spectroscopy, *Spectrochim. Acta B* 60 (2005) 1564–1572.
  - [50] V.S. Burakov, V.V. Kiris, S.N. Raikov, Optimization of procedure of spectrochemical detection of chlorine contents in cement materials, *J. Appl. Spectrosc.* 74 (2007) 321–327.
  - [51] S.M. Pershin, Transformation of the optical spectrum of a laser plasma when a surface is irradiated with a double pulse, *Sov. J. Quantum Electron* 19 (1989) 215–218.
  - [52] V.A. Rozantsev, A.D. Shirokanov, A.A. Yankovsky, Effect of the time interval between single pulses on the character of the laser plasma spectrum, *J. Appl. Spectrosc.* 59 (1994) 797–800.
  - [53] A. De Giacomo, M. Dell'Aglio, D. Bruno, R. Gaudiuso, O. De Pascale, Experimental and theoretical comparison of single- and double-pulse LIBS on metallic samples, *Spectrochim. Acta B* 63 (2008) 805–816.
  - [54] R.S. Brickley, D.J. Brown, J.E. Barefield, S.M. Clegg, Intact soil core total, inorganic, and organic carbon measurement using laser-induced breakdown spectroscopy, *Soil Sci. Soc. Am. J.* 75 (2011) 1006–1018.
  - [55] R.S. Brickley, D.J. Brown, P.J. Turk, S.M. Clegg, Improved intact soil-core carbon determination applying regression shrinkage and variable selection techniques to complete spectrum laser-induced breakdown spectroscopy (LIBS), *Appl. Spectrosc.* 67 (2013) 1185–1199.
  - [56] M.Z. Martin, M.A. Mayes, K.R. Heal, D.J. Brice, S.D. Wullschlegel, Investigation of laser-induced breakdown spectroscopy and multivariate analysis for differentiating inorganic and organic C in a variety of soils, *Spectrochim. Acta B* 87 (2013) 100–107, <http://dx.doi.org/10.1016/j.sab.2013.05.026>.
  - [57] R.C. Izaurre, C.W. Rice, L. Wielopolski, M.H. Ebinger, J.B. Reeves III, A.M. Thomson, R.N. Harris, B. Francis, S. Mitra, A.G. Rappaport, J.D. Etchevers, K.D. Sayre, B. Govaerts, G.W. McCarty, Evaluation of three field-based methods for quantifying soil carbon, *PLoS ONE* 8 (2013) e55560, <http://dx.doi.org/10.1371/journal.pone.0055560>.



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