

# A Survey of Recent Applications of Laser-induced Breakdown Spectroscopy (LIBS) to Soil Analysis

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## Introduction

The growth of the world agriculture economy largely depends on the efforts of scientists, operators and producers in investigating the proper use of innovative technologies in agricultural sciences. In particular, the implementation of modern precision agriculture, i.e. a management practice that takes into account the spatial variability of agricultural areas, implies the rationalization of the use of soils and inputs such as fertilizers, so to obtain a more sustainable production. An important issue of precision agriculture is the development and availability of sensors and portable equipments that can enable the fast analysis of macro and micronutrients and inorganic and organic pollutants [1] directly in the field. In particular, photonic devices, thanks to their high potential for miniaturization and reasonable costs involved in sample preparation and analysis, appear a very promising tool to develop instrumentations viable for field application.

Traditional analytical techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS), ICP-optical emission spectroscopy (ICP-OES) and flame atomic absorption spectrometry (FAAS), have been widely used for the multi-elemental analysis of soils. However, these techniques generally involve long and complex sample preparation steps and the production of chemical waste, thus they do not respond efficiently to the demand of low-cost and real-time measurements for soils. Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectrometry based on plasma generation by high power pulses [2,3], which features several advantages in its use in various sectors such as soil analysis. These include the potential for simultaneous multi-elemental analysis, minimal and fast sample preparation and processing, no production of polluting waste and relatively low cost compared to traditional techniques. Further, a specific feature that makes LIBS attractive for analyses in the field is the availability of system configurations enabling the construction of portable equipments for *in-situ* measurements [4,5].

Since the early days of LIBS, soils have been among the most popularly studied agricultural materials for the measurements of plant major and minor nutrients, including carbon, nitrogen, phosphorus and phytotoxic trace elements. In the last decade, a few reviews have surveyed the application of LIBS to specific issues related to soils. These include: the elemental analysis of soils and other agricultural products [6]; the quantitative measure of soil C components with emphasis on soil organic C [7]; in combination with laser-induced fluorescence spectroscopy (LIFS), the evaluation of the humification degree of soil organic matter directly in intact untreated whole soils [8]; the recent progress of applications to the analysis of soils and fertilizers [9].

The aim of this commentary is to briefly focus on the most recent progress achieved by LIBS technology in the analysis of soils and provide insights into new research and application trends.

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## Brief Introduction to LIBS Instrumentation and Methodology

A conventional LIBS equipment consists of a laser, a spectrometer, a number of lenses and optical fibers, a data acquisition system, and a control and synchronization system between the laser and the spectrometer. The most commonly used laser is the garnet yttrium doped neodymium (Nd: YAG) solid state laser that emits radiation at the characteristic wavelength of 1064 nm. The high-power laser beam is focused on the sample causing the ablation of a small portion of matter, of the order of nanograms, that generates a plasma plume. The detection of the light emitted by the plasma is obtained by a charge-coupled device (CCD) detector or an amplified intensified (ICCD) detector that allows to measure the evolution of the light emitted by the plasma. The elements present in the sample produce unique spectral atomic and ionic emission lines that can be detected by commercial spectrometers commonly covering a spectral range between 190 and 900 nm, which allows the univocal identification and quantification of almost any element of the periodic table, thus representing a robust tool for material analysis [2,3]. Although the intensities of the elemental emission lines featured by typical LIBS spectra should be proportional to the concentrations of the relevant elements in the sample, this relationship is not always linear due to a number of effects, named "matrix effects", which are related to differences in material matrices, including hardness, chemical composition, density, reflectivity, etc.

Although LIBS is often considered to be less sensitive than other spectroscopic analytical techniques, in recent decades it has become popular and successful in several fields of research and practical applications [10]. Further, a growing interest exists in the development of new instrumentations and analytical approaches in order to improve LIBS sensitivity and detection limits and reduces the

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effects of sample matrix, and testing both well-established and novel chemometric approaches [10]. In particular, in recent years double pulse (DP)-LIBS, which is able to improve the signal level and the elemental limit of detection (LOD) has been one of the most studied systems [11]. In this arrangement a second laser pulse is triggered after a delay time (interpulse) from the first laser pulse by re-exciting either the region where the plasma is generated by the first pulse or, in some cases, the surface of the sample [2,3].

## Recent LIBS Applications to Soil Analysis

### Plant macro and micronutrients

Recently, the performance of DP-LIBS, i.e. the spectral intensity, signal stability and detection sensitivity achieved, was compared to single pulse (SP)-LIBS in analysing a number of plant nutrient elements in 63 soil samples [12]. The best method for the quantitative determination of the macronutrients K, Ca, Mg and the micronutrients Fe, Mn, Na in soil resulted to be DP-LIBS coupled with partial least square regression (PLSR) analysis.

The matrix and soil heterogeneity effects were evaluated in measuring the Ca content in soil at the micrometric scale by comparing the performance of univariate and multivariate treatments of LIBS data to that of ICP-OES and X-ray fluorescence (XRF) techniques [13]. The calibration models were constructed using 16 certified reference soils, whereas outliers were classified and identified using principal component analysis (PCA) of appropriately pre-treated data. Further, the Ca content was validated by PLSR on a set of 60 different soils of highly heterogeneous matrices and a rough classification of soils based on a Ca content of < 1%, 1-3% and > 3% was achieved by PCA of LIBS data.

### Phytotoxic trace elements

Recently, a simple and low cost soil pretreatment method, named solid-liquid-solid transformation and consisting in subjecting soil samples to ultrasonic vibration followed by centrifugation and subsequent deposition and drying on a glass slide, was proposed to extract available Cd and Pb from soil before measuring their content by LIBS [14]. After optimization of operational conditions, a value of  $r^2 > 0.98$  was featured by calibration curves and LODs much lower than those obtained by conventional analysis were achieved.

Also recently, a homemade, relatively cheap and easy handling tunable continuum wave-diode laser (CW-DL) operating in the violet region (405 nm) was developed in the attempt to enhance the sensitivity of LIF-assisted LIBS for Pb detection in soil by improving the emission intensity of the Pb I transition occurring at 405.78 nm [15]. When the CW-DL device was directed radially to the plasma plume coupled to a DP-LIBS system in a collinear configuration, an increase of about 100% of the Pb I emission intensity was achieved with respect to the DP-LIBS system used alone. This result was ascribed to the pumping of the CW-DL beam on the specific Pb electronic transition at the optimal temperature of 10000 K. Thus, the CW-DL device showed to be a more viable tool than the very expensive optical parametric oscillators (OPO) commonly used in a LIBS-LIF apparatus to re-excite a transition of the element of interest in the plasma in order to increase its LIBS signal intensity.

The analytical performance of univariate and multivariate calibration models was evaluated at various laser wavelengths in

investigating the matrix effects and spectral interferences by major and trace components affecting Pb determination by LIBS in various types of soil containing from 8.5 to 280  $\mu\text{g g}^{-1}$  of Pb [16]. The use of the 3rd harmonic of the Nd: YAG laser combined with calibration by principal components regression (PCR) model using three principal components provided the best analytical results. Further, a good agreement was achieved between the Pb content measured by LIBS ( $46 \pm 5 \mu\text{g g}^{-1}$ ) and XRF ( $42.1 \pm 3.3 \mu\text{g g}^{-1}$ ) in an unknown soil sample.

In another recent work aiming to improve the LOD of heavy metals in various soil samples, LIBS emission spectra were acquired in the presence and absence of an external magnetic field applied transversally to the plasma plume [17]. In the presence of the magnetic field, the signal intensity of Cr was enhanced by a factor up to about 8, which was ascribed to the magnetic confinement of the laser-generated plasma, and its LOD was improved from 18.2 to 7.7  $\text{mg Kg}^{-1}$ .

A novel LIBS approach was developed recently with the aim of reducing the interference of matrix effects in the rapid quantification of Cu, Ni, Cr and Pb in 169 agricultural soils [18]. Two multivariate methods, i.e. least absolute shrinkage and selection operator (LASSO) and PCR, were used and both resulted efficient in reducing matrix interference by achieving a normalized root mean square error (RMSE) lower than 11% for the four elements analysed.

Further, a novel sample pretreatment was tested in order to improve LIBS sensitivity in the analysis of water-soluble and exchangeable Cd in soils that were laboratory-contaminated with Cd in the slurry state [19]. The method consisted in enriching Cd by passage through a cation exchange resin and using a sample container provided with a device for the spatial confinement of the laser plasma in the LIBS measurement, thus simplifying sample pretreatment and avoiding the problem of soil splattering during analysis. The intensity of the three emission lines of Cd II at 214.4 and 226.5 nm and Cd I at 228.76 nm were enhanced significantly with respect to the traditional pellet method. Further, the calibration curve constructed using the signal intensity of Cd II line at 226.5 nm yielded a  $r^2 = 0.9715$  with a LOD of 0.132  $\text{mg Kg}^{-1}$  for Cd, which was largely improved with respect to that obtained by the traditional approach.

### Miscellaneous soil properties

Very recently, LIBS and FAAS were used to investigate the role of the humic acid (HA) and fulvic acid (FA) soil organic fractions in the transport of Al and Fe to deeper soil profiles during the process of podzolization in Amazonian soils [20]. Both organic fractions were shown to be involved with FA having a predominant role in the translocation of Al and HA in that of Fe.

In another very recent work, LIBS has been used for the rapid, high-resolution ( $\sim 100 \mu\text{m}$ ), multi-elemental imaging of both organic and inorganic components in the highly dynamic and chemically complex root-rhizosphere-soil continuum system constituted of a switchgrass plant assemblage grown on a sandy loam Alfisol in a compact rhizotron [21]. Intact live root-soil frozen samples were extracted by appropriate devices and broadband SP-LIBS spectra were collected from a raster of evenly-spaced spots across a large root-soil surface. Then, the spectra were XY-plotted to yield the 2D imaging of the distribution of 17 macro and micronutrient elements and matrix components. A specifically developed open-source Python module based on PCA of normalized spectral intensities was applied

to rapidly process and investigate LIBS raster data. The procedure allowed to discriminate soil mineral grains, root fragments and other organic residues favoring microbial growth in the rhizosphere region. Further, the extension of the image analysis protocol developed in this work to other root-soil investigations, such as tracking nutrient flow within active root biomass, was also discussed.

### Portable and Standoff LIBS in Soil Analysis

A great interest has been and is devoted to the miniaturization of LIBS system components in order to develop portable equipments able to perform soil analysis *in-situ* with increased stability and sensitivity of the measurements [4,5]. Recently, a stand off LIBS system operating in N<sub>2</sub> and He ambient gases at atmospheric and low pressures was used for the *in-situ* detection of Cs in waters and soils in the area nearby the Fukushima Nuclear Power Station in Japan [22]. The emission spectra acquired at the pressure of 0.5 kPa N<sub>2</sub> yielded a LOD of 0.3 μg g<sup>-1</sup> for Cs in soil samples. Thus, the stand off LIBS system employed represented a viable, practical and mobile *in situ* alternative to the commonly employed gamma-ray spectroscopy using a Ge Detector.

In the same year, a homemade LIBS system that could operate either as a mobile equipment in the laboratory or as a handheld instrument in the field was used for heavy metals detection in soil [23]. In particular, the Cu, Pb and Zn contents were determined by constructing two calibration curves using ICP-MS as the reference technique. Then, soil samples were classified into two different groups by PCA. The equipment was able to analyse semi quantitatively the elements Cu, Pb and Zn with LODs below 10 mgKg<sup>-1</sup> in the laboratory, whereas spectral stability was hard to be achieved when the handheld instrument was used in the field. However, the emission signals of Cu and Zn improved significantly with a RMSE lower than 20% when Si and Fe lines were used as internal standards.

More recently, the performance of three techniques, i.e. Vis-near infrared spectroscopy (NIRS), LIBS and combined Vis-NIRS-LIBS, were evaluated comparatively for the *in-situ* analysis of total C (TC), inorganic C (IC) and organic C (OC) in soil profiles [24]. The application of three multivariate variable selection and regression models to analytical data showed that the multivariate regression with covariance estimation (MRCE) model yielded the highest accuracy for soil C predictions. In particular, the best predictions were provided by LIBS for IC, Vis-NIR for OC and combined Vis-NIRS-LIBS data for TC. However, further testing on soils with a greater diversity of OC content are needed to confirm the analytical potential of the two combined techniques for soil C measurements *in-situ*.

### Conclusions and Perspectives

In recent years research aspects that mostly have caught the attention in exploring soils by LIBS were oriented to improve various performance factors of the technique. Some significant advances have been achieved in LOD improvements of various elements, optimization of the S/N ratio with increase of signal intensity and application of modern powerful chemometric methods. However, other aspects such as the efficient use of on-line and *in-situ* LIBS approaches still remain a challenging research matter. In particular, although the dynamics of matrix effects have been studied widely, more in-depth studies are still required to eliminate, or at least minimize this relevant analytical problem. For example, the achievement of representative results with reduced variability within a soil sample would require many repetitive measurements at different positions on the soil pellet.

Further, different matrix-dependent calibration models should be applied to each soil class to improve the correct element quantification by LIBS.

A number of novel experimental setups have been proposed recently to improve LIBS sensitivity, i.e. the LOD of an element in a sample. These include femtosecond (fs) LIBS, nanoparticle-enhanced (NE) LIBS, micro-LIBS, LIBS assisted by LIF (LIBS-LIF), resonance enhanced LIBS (RELBS) or resonant LIBS (RLBS), microwave-assisted (MA)-LIBS and LIBS under controlled atmosphere. For example, the insertion of resonant photons in the plasma can promote a specific electronic transition, thus favoring directly or indirectly the transition of the target analyte, so improving the LOD of some contaminants and other elements of interest which would be otherwise subject to interferences in the LIBS spectrum.

Further, the capacity of LIBS to provide a real-time imaging of the complex root-soil system with simultaneous multi-element, including light elements, acquisition appears very promising for a possible field deployment to evaluate fertilizer application impacts and develop environmental remediation strategies for reclaiming waste-contaminated sites. In the future, very important will be to build a software that can allow the easy collection of metadata, the construction and export of elemental distribution element maps within soils and spectral data at individual locations, and import data into third party pedological software to achieve advanced analytical results.

The great progress achieved in LIBS instrumentation and data processing applied to other sectors is reasonably expected to be extended to the study of soils and promote the development of new approaches able to solve and overcome the various drawbacks, problems and limitations still existing in the efficient application of LIBS to the agriculture sector. When compared to previous years, a significant increase of publications related to the use of LIBS in agricultural sciences and applications has occurred especially in the last 2 years, which indicates a strong upward trend for the incoming years.

### Competing Interests

The author declare that there is no competing interests regarding the publication of this article.

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