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Novel estimation of the humification degree of soil organic matter by laser-induced breakdown spectroscopy

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ABSTRACT

Soil organic matter (SOM) constitutes an important reservoir of terrestrial carbon and can be considered an alternative for atmospheric carbon storage, contributing to global warming mitigation. Soil management can favor atmospheric carbon incorporation into SOM or its release from SOM to atmosphere. Thus, the evaluation of the humification degree (HD), which is an indication of the recalcitrance of SOM, can provide an estimation of the capacity of carbon sequestration by soils under various managements. The HD of SOM can be estimated by using various analytical techniques including fluorescence spectroscopy. In the present work, the potential of laser-induced breakdown spectroscopy (LIBS) to estimate the HD of SOM was evaluated for the first time. Intensities of emission lines of Al, Mg and Ca from LIBS spectra showing correlation with fluorescence emissions determined by laser-induced fluorescence spectroscopy (LIFS) reference technique were used to obtain a multivaried calibration model based on the k-nearest neighbor (k-NN) method. The values predicted by the proposed model (A-LIBS) showed strong correlation with LIFS results with a Pearson's coefficient of 0.87. The HD of SOM obtained after normalizing A-LIBS by total carbon in the sample showed a strong correlation to that determined by LIFS (0.94), thus suggesting the great potential of LIBS for this novel application.

1. Introduction

Soil organic matter (SOM) represents the main reservoir of terrestrial carbon and can be considered an important alternative to reduce atmospheric carbon emissions. It is estimated that 2/3 of terrestrial carbon is contained in SOM. However, unlike the carbon in fossil fuels (inactive unless the burn occurs) the carbon in SOM can be converted to atmospheric carbon by soil micro-organisms and chemical decomposition, thus increasing the atmospheric CO_2 content [1,2]. Several research groups have observed that some practices of soil management can contribute to atmospheric carbon sequestration and to increase carbon stock in the soil [3–6]. Therefore, the study of soil management effects on SOM stability is useful to help establishing the most appropriate management aiming to minimize CO_2 emissions and improve soil quality.

Most carbon in SOM is contained in humic and non-humic substances; thus, carbon stability is related to the humification degree (HD) of SOM, in that highly humified SOM fractions, such as humic substances (HS), are more stable compared to less humified ones. In the humification process the concentration of recalcitrant chemical structures, such as complex conjugated aromatic rings and long aliphatic rings, increases [7], whereas non-humic fraction possesses a simpler chemical structure. Analytical techniques such as fluorescence spectroscopy and nuclear magnetic resonance (NMR) have been used to assess the HD of HS [8–14]. Further, analytical techniques able to identify specific radicals present on aromatic structures (e.g. semiquinones types), such as electron paramagnetic resonance (EPR), have been successfully applied [15,16].

Nevertheless, the determination of HD using the analytical techniques mentioned above generally requires a complex laboratory sample pretreatment, which may last up to fifteen days. Further, the laboratory procedure requires the preliminary isolation of HS, which represents only a fraction of the bulk SOM. Thereby, the adoption of these methods does not allow the estimation of whole SOM stability.

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Further, the presence of Fe^{3+} in HS represents a drawback in the application of NMR and EPR techniques [7].

To assess the HD of SOM, Milori et al. [17] have introduced a humification index, denominated H_{LIFS}, that is the ratio between the integrated area under the emissions fluorescence spectra recorded at an excitation wavelength of 465 nm, and the percentage of the total carbon in the whole soil sample (fluorescence area/carbon%). The authors showed a close and direct correlation of H_{LIFS} with aromaticity assessed by NMR and free radical semiquinone content assessed by EPR for soil humic acids (HAs). The authors thus proposed that H_{LIFS} can be used as an indicator of the chemical complexity of SOM and, possibly, of its stability/recalcitrance. Although this method has very interesting features based on the direct, fast and clean determination of fluorescence spectra, it depends on the percentage of total carbon, which is usually obtained through elemental (CHNS) analysis, thus increasing the time and cost of analysis.

Laser-induced breakdown spectroscopy (LIBS) is an emerging analytical technique capable of performing multi-elemental direct analysis without any laboratory sample pre-treatment and having the potential to perform analysis *in situ* [18,19]. In a LIBS experiment a high-energy laser pulse irradiates the target and the energy absorbed by the portion test causes a local heating of the material that results in its evaporation or sublimation. The high temperature of the ablated material generates a small plasma plume and, as a result of the plasma temperature, the ablated material breaks down into excited atomic and ionic species. During the plasma cooling, the excited species return to their lower energy state emitting electromagnetic radiation at characteristic wavelengths [20]. In a LIBS spectrum the measurement of the characteristic emission wavelengths provides qualitative information about the elemental composition of the sample, whereas the intensities of the signals can be used for quantitative determinations [19,20]. The LIBS potential for the analysis of organic compounds has also been explored recently [21–23] by using the emission lines of elements that are commonly present in organic compounds, such as the predominant C, H, P, O and N [23].

In the present work the potential of LIBS to provide the HD of bulk SOM was evaluated. To this purpose, the correlation between LIBS elemental emission line intensities and the fluorescence area of integrated laser-induced fluorescence spectra (LIFS) was investigated. A value equivalent to the LIFS fluorescence area determined from the LIBS spectrum intensities, named A-LIBS, was normalized by the total carbon content in the laboratory sample, which was determined using the same LIBS spectrum.

2. Materials & methods

Fifty-six soil samples, classified as red yellow argisol containing 67.5 g/kg of sand, 17.6 g/kg of silt and 14.8 g/kg of clay, were collected at five locations at six different depths: 0-5, 5-10, 10-20, 20-30, 30-50, and 50-80 cm from two different sugar cane management areas, either under raw cane (RC) mechanical harvesting, or under burned cane (BC) manual harvesting after a controlled burning procedure.

The soil laboratory samples were homogenized using a mortar and a pestle to obtain particle sizes smaller than 0.15 mm. To obtain soil pellets (portion test) an amount of 0.5 g of each laboratory sample was submitted to 8 tons of pressure. Three pellets were made for each laboratory sample. The LIFS and LIBS spectra were obtained from the pellets.

2.1. LIFS measurements

The LIFS spectra were measured on a lab-assembled instrument that includes a continuous wave laser at a wavelength of 405 nm, a bifurcated optical bundle fiber and a spectrometer. The laser emission was conducted on the pellet surface through six external optical fibers, and the fluorescence emission resulting from the decay of excited species was transferred to the spectrometer through a central optical fiber bundle. A computer assisted in recording the spectra and adjusting the measurement conditions. The measurement range was from 420 nm to 800 nm, the maximum intensity of emission was 4000 counts, and the integration time, average and boxcar selected were 400 ms, 3 and 3, respectively, for all measurements. Ten spectra were acquired for each portion test by focusing the continuous laser radiation on different 3.14 mm^2 sites of the pellet. As three pellets were examined for each laboratory sample, three sites were irradiated in two pellets and four sites in the third pellet. The ten obtained spectra were then averaged to have a representative spectrum for each sample.

2.2. LIBS measurements

As LIFS technique performs non destructive analysis, the surfaces of pellets remained unchanged; thus, the LIBS spectra were measured on the same pellets previously submitted to LIFS analysis.

Three pellets were examined for each laboratory sample and twenty sites were irradiated in each pellet, ten sites for each face. Thus, a total of sixty spectra were obtained from each sample. Each site was irradiated employing two consecutives laser pulses, so that the spectrum obtained corresponded to the instrumental average of two laser pulses. A previous laser pulse was always used to clear the pellet surface before obtaining the experimental spectrum. The average of spectra from each pellet (40 pulses) was considered as a single measurement, and the average (and respective standard deviation) of spectra of the three pellets for each laboratory sample was used for the proposed predictions.

The LIBS spectra were obtained using a system model LIBS2500 (Ocean Optics, USA). This system includes seven spectrometers that provide a resolution of ~0.1 nm (FWHM) for the spectral analysis ranging from 188 to 980 nm, a Q-switched Nd:YAG laser at 1064 nm (Quantel, Big Sky Laser Ultra50), an ablation chamber, a lens for laser focalization, and an optical system to collect plasma emission and address it to the spectrometers. A laser pulse of 50 mJ energy and a duration of 8 ns was used for all measurements. The laser fluence was 1.2×10^3 J cm^{-2} and the diameter of the spot on soil pellets was 73 mm. The delay time (relative to a Q-switch delay) and integration time used were 10 μs and 2 ms respectively, which are instrumental fixed conditions. The distance between the radiation collecting lens and plasma sampling was fixed at about 1 cm.

The obtained spectra were individually normalized by dividing each point of the spectrum by the area calculated under the corresponding spectrum. The area was calculated separately for each spectrometer and only the spectra recorded by the first four spectrometers were used. Therefore, the spectral evaluated wavelength ranged from 190.8 to 500.6 nm. After normalization, the spectral offset was corrected from the beginning of the spectrum with an average of 30 intensities values calculated from a pure noise region. Before performing spectra average, data of LIBS emissions resulting from measurements of each pellet were tested for normality and the Grubb's test was applied for outlier's exclusion. An average was obtained for each pellet and the sample values and respective standard deviations were obtained averaging the values of three pellets.

2.3. Total carbon determination

The carbon content of laboratory samples was obtained by two analytical techniques: CHNS analyzer and LIBS. The carbon determination by CHNS was performed using a 2400 CHNS analyzer series II from Perkin-Elmer. The soil laboratory samples were weighed directly in consumable tin capsules, which were closed and introduced in the instrument furnace. A 10-mg mass of each laboratory sample was measured using a microbalance PerkinElmer AD-6 Auto Balance Controller, which is connected to the 2400 CHNS for direct mass acquisition.