Fluorescence spectroscopy of soil pellets : The use of CP/PARAFAC.

Stéphane Mounier (1), Gustavo NICOLODELI (2), Roland REDON (1), Kalhed HACHEROUF (1), and Debora M B P MILORI (2)

(1) University of Toulon, Department of Chemistry, BP20132, 83957 La Garde Cedex, France (mounier@univ-tln.fr), (2) Embrapa Agricultural Instrumentation, P.O. Box 741, 13561-206 São Carlos, SP, Brazil

Fluorescence spectroscopy is one of the most sensitive techniques available for analytical purposes. It is relatively easy to implement, phenomenologically straightforward and well investigated. Largely non-invasive and fast, so that it can be useful for environmental applications.

Fluorescence phenomenon is highly probable in molecular systems containing atoms with lone pairs of electrons such as C=O, aromatic, phenolic, quinone and more rigid unsaturated conjugated systems. These functional groups are present in humic substances (HS) from soils (Senesi, 1990; N. Senesi et al., 1991) and represent the main fluorophors of Soil Organic Matter (SOM). The extension of the conjugated electronic system, the level of heteroatom substitution and type and number of substituting groups under the aromatic rings strongly affect the intensity and wavelength of molecular fluorescence. However, to analyse the SOM it is generally done a chemical extraction that allows measuring the fluorescence response of the liquid extract. To avoid this fractionation of the SOM, Milori et al. (2006) proposed the application of laser induced fluorescence spectroscopy (LIFS) in whole soil. This work intends to assess the technical feasibility of 3D fluorescence spectroscopy using lamp for excitation to analyse solids opaque samples prepared with different substances.

Seventy four (74) solid samples were prepared from different mixtures of boric acid (BA), humic substance acid and tryptophan (TRP) powder. The compounds were mixture and a pellet was done by using pressure (8 ton). The pellets were measured using a spectrofluorimeter HITACHI F4500, and a 3D fluorescence tensor was done from emission spectra (200-600 nm) with excitation range from 200 to 500 nm. The acquisition parameters were: step at 5 nm, scan speed at 2400 nm.min-1, response time at 0.1 s, excitation and emission slits at 5 nm and photomultiplier voltage at 700 V. Furthermore, measures of Laser-induced Fluorescence were performed in pellets (boric and humic acids mixture) using a portable system built by Embrapa Instrumentation. It comprises a diode laser (Coherent - CUBE) emitting at 405 nm (50 mW), and the detection of emission by a high sensitivity mini-spectrometer (USB4000 - Ocean Optics) using a range from 440 to 800 nm. In first step, the 3D tensors were then treated by the CP/PARAFAC algorithm to decompose the signal response after removing the diffusion signal : three components were extracted with a CORCONDIA over 60%.

The first component can be associate an artefact of the measurement or boric acid fluorescence, the second and third component could the related to the two different fluorescence contributions of tryptophan molecule, one with central excitation/emission in 290/360 nm and other in 350/465 nm.

The presence of a small quantity (i.e. few percent in mass) of humic acid (HA) is quenching drastically the TRP fluorescence. Complementary, measurements will be performed to understand this behaviour taking in account the absorption wavelength by the surface (colour) and by measuring the time life fluorescence of the samples. Humic acid fluorescence in pellets (BA and HA) cannot be observed using lamp + monochromator excitation due to low intensity of source. The same pellets were measure using LIFS system, and fluorescence intensity increased as a function of concentration of HA until occur the inner filter effect from 300 ppm, similar to the behaviour of HA in solution. Even whether solid surface measurements are easier, understanding is not yet clear. More investigation needs to be done. Moreover, it should be important to know if the use of CP/PARAFAC decomposition for such data is relevant with the trilinear model.

References

Milori, D.M.B.P., Galeti, H.V.A., Martin-Neto, L., Dieckow, J., González-Pérez, M., Bayer, C., Salton, J., 2006. Organic Matter Study of Whole Soil Samples Using Laser-Induced Fluorescence Spectroscopy. Soil Science Society of America Journal 70, 57.

N. Senesi, TM, M., MR, P., Brunetti., G., 1991. Characterization, differentiation and classification of humic substances by fluorescence spectroscopy. Soil Science 152, 259–271.

Senesi, N., 1990. Molecular and quantitative aspects of the chemistry of fulvic acid and its interactions with metal ions and organic chemicals. Analytica Chimica Acta 232, 77–106.