Composition of the humin fraction of *Terra Preta de Índios* soils by NMR and multivariate curve resolution

E. H. Novotny (1,2), M. H. B. Hayes (3), G. Song (4), E. R. deAzevedo (5), and T. J. Bonagamba (6)

(1) Embrapa Solos, Rio de Janeiro-RJ, Brazil (etelvino@cnps.embrapa.br/+55 21 2274-5291), (2) Chemical and Environmental Sciences, University of Limerick, Ireland (etelvino@cnps.embrapa.br/+353 61 20 25 72), (3) Chemical and Environmental Sciences, University of Limerick, Ireland (michael.h.hayes@ul.ie/+353 61 20 25 72), (4) Department of Civil, Environmental, and Sustainable Engineering, Ira A. Fulton School of Engineering, Arizona State University, USA (gxsong@gmail.com/+1-480-797-1291), (5) Instituto de Física de São Carlos - USP São Carlos-SP, Brazil (azevedo@ifsc.usp.br/+55 16 3373-9876), (6) Instituto de Física de São Carlos - USP São Carlos-SP, Brazil (tito@ifsc.usp.br/+55 16 3373-9876)

Most of the soils in the Amazon Region are acid, with low cation-exchange capacity (CEC) values, low fertility, and low production potential. There exists a class soils in this environment that have an archeo-anthropedogenic horizon of pre-Columbian origin, called "*Terra Preta de Índios*" (TPI), also known as Amazonian Dark Earths. These soils are characterized by higher fertility and more stable organic matter (OM) than the surrounding soils.

The high fertility of TPI, and especially their sustainability, is attributed to the high levels of OM and to their physical-chemical properties. Up to 35-45% of the organic C in TPI is in the form of pyrogenic carbon (black carbon), compared to 14% in surrounding soils lacking an archeo-anthropedogenic horizon.

Pyrogenic carbon derived from the partial carbonization of ligno-cellulosic materials, is composed of hydrogen-deficient condensed aromatic structures and, as the result of chemical and biochemical transformations, has a high charge density from carboxylic groups linked mainly to the aromatic core.

Humin is the most recalcitrant and least understood fraction of soil OM. By definition, humin is the fraction that is not soluble in traditional aqueous alkaline soil extractants. It represents more than 50% of the soil organic carbon (OC) in mineral soils and more than 70% of the OC of lithified sediments, and is therefore the most important pool of the soil OM. However, for a study of humin by NMR it is necessary to isolate it and to achieve a degree of fractionation/purification. In this regard, an appropriate procedure[1] has been applied to two soil samples from TPI and the material obtained was studied by solid state ^{13}C NMR. The data analyses were carried out by Multivariate Curve Resolution (MCR).

Results and Discussion

MCR resolved the spectral matrix into three components, and these can be attributed to wood, humin, and oxidised charcoal materials

The spectrum for the wood component agrees very well with that of eucalyptus wood. On the other hand, the humin spectrum shows an intense signal in the alkyl region (0-40 ppm) with a prominent signal for crystalline polymethylene at 33 ppm. These signals, in association with the carboxyl signal (173 ppm), indicate fatty acid origins for these components. Additionally, some altered aromatic structures (a broad and featureless signal centred at 130 ppm) and cellulosic material (110 and 70 ppm) were also evident. The broad signal at 54 ppm was probably from N-alkyl compounds from proteinaceous material since the corresponding O-aryl signal from the alternative methoxyl contribution was lacking. Finally, the oxidised char component was characterised by the broad and featureless signal at 128 ppm and the carboxyl at 172 ppm. The shoulder at 167 ppm gave evidence for carboxyl directly attached to the aromatic backbone. This char component also had minor contributions from aliphatic compounds, such as alkyl, N-alkyl, methoxyl, and carbohydrates.

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[1] Song, G., Novotny, E.H., Simpson, A., Clapp, C.E. and Hayes, M.H.B., 2008. European Journal of Soil Science, 59: 505–516.

With regard to the estimated concentrations of each of these components, the coarse char samples and the residual humin (before and after DMSO/H_2SO_4 extraction) presented a higher content of unaltered wood (cellulose and lignin) material.

The humin extracted by DMSO/H_2SO_4 was very rich in long chain aliphatic compounds (alkyl groups: 0-40 ppm). This lipidic fraction was also extracted by the alkali urea treatment and by soil dispersion using ultrasounic vibration. Greater amounts of oxidised char were also isolated following the ultrasonic treatment. This component remained in the residual humin, and it was also abundant in the coarse char fraction, indicating that the solvent systems adopted were unable to solubilise these materials. The extractable humin probably corresponds to fatty acids associated with the clay fraction and the un-extractable fraction was probably composed of particulate char (partially, and oxidised) and vegetable tissues.

In conclusion, the extractable humin in these soils is mainly composed of hydrophobic compounds strongly associated with the mineral fraction. The DMSO/H_2SO_4 solvent is very efficient for solubilising these lipidic compounds. On the other hand, the disruption of the clay aggregates, by ultrasonication, allows additional oxidised char to be released and solubilised by the DMSO/acid and by the alkaline urea systems.