

CHARCOAL AS IMPORTANT FACTOR IN SOIL ORGANIC MATTER FORMATION IN BRAZILIAN ECOSYSTEMS

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Ferralsols cover almost 40% of Brazil and can be found under a wide variety of vegetation and in many different landscapes. Some of them exhibit a high content of organic carbon (umbric epipedon) and thus represent an important sink of stable C. Also, many of them contain charcoal fragments suggesting that frequent (natural) fires affected their organic matter (OM) composition. However, in spite of many efforts, the composition of its OM and the mechanisms involved in its stabilization are still to be explored (Marques *et al.*, 2011).

The present study focuses on SOM characterization of Umbric Ferralsols for a better understanding of how charred material influences the humification processes and how it affects the C sequestration potential of such soils.

Soil samples were collected from three Umbric Ferralsols of Viracopos (UF-Vr), Atibaia (UF-At) and Chapecó (UF-Ch), Southern Brazil. During sampling, charred residues were found in the UF-Vr distributed irregularly and present at all depths along the profile, with more elevated density between 65-80 cm and 100 cm in depth.

To study the nature of their organic matter, we performed a characterization of their chemical composition by solid-state ¹³C NMR spectroscopy after their demineralization with 10% HF (Gonçalves *et al.*, 2003). Five chemical shift regions were distinguished (Knicker and Lüdemann, 1995): alkyl C (0-45 ppm), N-alkyl C (45-60 ppm), O-alkyl C (60-110 ppm), aryl C (110-160 ppm), carboxyl C (160-245 ppm).

In order to identify contributions of black carbon, the HF-treated samples were subjected to chemical oxidation (K₂Cr₂O₇, 60 °C, 6h). The aromatic C content remaining in the residue was assigned to pyrogenic organic material and quantified by NMR spectroscopy (Knicker *et al.*, 2007).

The solid-state ¹³C-NMR spectra of the top horizons from UF-Ch showed sufficiently high signal to noise ratios for integration, no spectra could be obtained from the deeper horizons. The first are dominated by a signal at 30 ppm in the region assigned to alkyl C in lipids and amino acids (45 - 0 ppm). Other major intensities are observed between 110 and 45 ppm, in the region of O/N-alkyl C (carbohydrates, amino acids) and carboxyl C (220 to 160

ppm). The missing of a clear signal in the region between 160 and 140 ppm (signal derives from aromatic or olefinic C) indicates that in this soil lignin has minor contributions to its aromatic C content. The contribution of aromatic C with depth may be explained with charcoal contributions. However, applying chemical oxidation with acid potassium dichromate could not confirm this assumption, possibly because it occurs in a highly oxidized form which can be attacked and destroyed by the strong acid. In the profile UF-Vr, however, between 12 and 83% of the total C resisted the harsh chemical treatment, confirming the presence of charcoal residues already visually observed during sampling. An increase of aromatic C with depth was also evident in the profile UF-At. In this soil, some of the C resisted the chemical treatment confirming the presence of charcoal residues. This is in line with the historical recurrent wild fire occurring in the Cerrado (savannah ecosystems).

Our results showed further that the presence of charred residues is an important factor to determining quality and quantity of humic material in the umbric epipedons of this kind of Ferralsols.

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