

TERRA PRETA (“DARK EARTH”) SOILS

Terra Preta De Índio “Dark Earth Soils”: Chemical and Spectroscopic Characterization of Humic Acids

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The HA of Amazonian dark earth soils (Terra Preta de Índio) from Brazilian territory were characterized using ultraviolet-visible, Fourier transform diffuse reflectance infrared, fluorescence excitation and emission, electron paramagnetic resonance, and nuclear magnetic resonance spectroscopy, thermogravimetric analysis, elemental composition, and measurement of acidity (total, carboxylic, phenolic). The HA fraction was extracted using the method of International Humic Substances Society. The samples were separated in 3 groups based on the corresponding land use of the area: anthropogenic soils under forest (SAF), anthropogenic soils under agricultural use (SAC), non-anthropogenic soils under forest (SNAF). The SNAF soils were representative of Amazonian soils. This way the SNAF group was a reference group for comparison purposes to the anthropogenic soil groups (SAF and SAC). The anthropogenic soil groups (SAF and SAC) showed better fertility characteristics than the non-anthropogenic soils (SNAF) (pH: SAF = 5.1, SAC = 5.4, SNAF = 4.4; base saturation [V%]: SAF = 59, SAC = 51, SNAF = 18; calculated cation exchange capacity [CEC]: SAF = 17.5, SAC = 17.2, SNAF = 9.5 cmol_c kg⁻¹; available P: SAF = 116, SAC = 291, SNAF = 5 mg kg⁻¹). In the SAF and SAC soil groups ~44% of the total carbon was found in the humin fraction, ~32% in the humic acid fraction, and ~13% in the fulvic acid fraction. These values for the SNAF soils were 49, 19, and 16%, respectively. The most relevant characteristics of the HA of anthropogenic soils, compared to the non-anthropogenic ones were their superior reactivity, stability, and humification degree. The HA of the SAF and SAC groups featured higher total acidity (SAF = 612, SAC = 712, SNAF = 575 cmol kg⁻¹) and carboxylic acidity (SAF = 435, SAC = 454, SNAF = 320 cmol kg⁻¹), higher concentration of organic free radicals (SAF = 4.07, SAC = 6.59, SNAF = 2.11 spin g⁻¹ 10¹⁷), higher thermogravimetric index (ITG) (SAF = 3.0, SAC = 3.3, SNAF = 2.3), lower E₄/E₆ ratio (SAF = 4.2, SAC = 4.2, SNAF = 6.0), higher aromaticity index (IADRIFT: SAF = 0.87, SAC = 0.85, SNAF = 0.77; NMR(%): SAF = 36, SAC = 39, SNAF = 25), higher hydrophobicity index (SAF = 0.37, SAC = 0.48, SNAF = 0.35), higher humification degree (A4/A1: SAF = 2.574, SAC = 3.313, SNAF = 1.713; I485/I400: SAF = 2.004, SAC = 2.161, SNAF = 1.510), and were more recalcitrant (recalcitrant C/labile C: SAF = 2.0, SAC = 2.0, SNAF = 1.0) than the HA of the SNAF group.