

Extraction and Characterisation of Humic Fraction from Amazonian Anthropogenic Dark Earths Soils (“Terra Preta de Índios”)

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1. INTRODUCTION

Humin, the humic fraction that is insoluble in water at all pH values, typically comprises more than 50% of soil organic matter (1). Because of the difficulties in isolation, humin compositions and properties have been less extensively studied than those of humic and fulvic acids (2). On the basis of the accepted definition, humin can include any humic-type substances that are not dissolved during exhaustive extractions with aqueous base.

A solvent system composed of a mixture of aqueous base/urea (0.1 M NaOH + 6 M urea, base/urea) has been reported to isolate material that would be classified as humin in the classical definition (3, 4, 5). Because urea is a powerful hydrogen bond breaker, it is considered that soil organic components were released from associations with humin materials either by the breaking of hydrogen bonds, or by the disruption of steric constraints by materials that had trapped the components released.

Dimethylsulfoxide (DMSO), a dipolar aprotic solvent, is an excellent solvent for cations but a poor solvent for anions (6). It is a good hydrogen bond breaker and the non-polar backbone (as distinct from the S=O face) of DMSO can be considered to have affinities for less polar humin components. A solvent mixture of DMSO with HCl (6%, v/v) was reported to have isolated less than 22% of humin material from soils (7, 8, 9). However H₂SO₄ is a very polar liquid with a high dielectric constant (~100), and due to the process of autoprotolysis (10), protons are highly mobile in H₂SO₄. This enables it to protonate the conjugate bases (carboxylates and phenolates), thereby increasing the solubility of the organic material (4, 5), since anions are weakly solvated in DMSO.

2. MATERIALS AND METHODS

The humin from three (samples 1, 2 and 3) Amazonian Dark Earths (“*Terra Preta de Índios*”), soils rich in pyrogenic carbon, was sequentially extracted using: 0.1 M NaOH (Humic Acids - HA); the soil residue was extracted with 0.1 M NaOH after the soil was dispersed by ultrasonication (HAD); then with base/urea (Humin - HuU); with a mixture of DMSO and H₂SO₄ (94:6, v/v) (HuDMSO); and finally the residue was treated with 10% HF (Hu). The coarse char fraction was carefully recovered from the soils by sieving (63 µm sieve) and sedimentation. Characterisations of the organic components of the humin fractions were carried out by Variable Amplitude Cross-Polarisation with Magic Angle Spinning (VACP/MAS) ¹³C Nuclear Magnetic Resonances spectroscopy, and additional experiments were carried out using the Chemical Shift Anisotropy (CSA) (spectra of C-sp³ only) and the Dipolar Dephasing (DD) (spectra of non-protonated and mobile C only) filters. The spectral data were analysed by Principal Component Analysis.

3. RESULTS AND DISCUSSION

Spectra are shown only for the HA and HAD samples (Figure 1). The HAD presents more aliphatic compounds, mainly crystalline poly-methylene structures (33 ppm) and with lesser of the amorphous structures (30 ppm). It is also richer in carbohydrates (102 and 73 ppm, as evidenced in the CSA spectra) and lignin residues (~150 ppm and 56 ppm, as evidenced in the DD spectra). These features indicate that the aggregate rupture releases relatively unaltered organic matter (cellulose and lignin derived materials) and also a

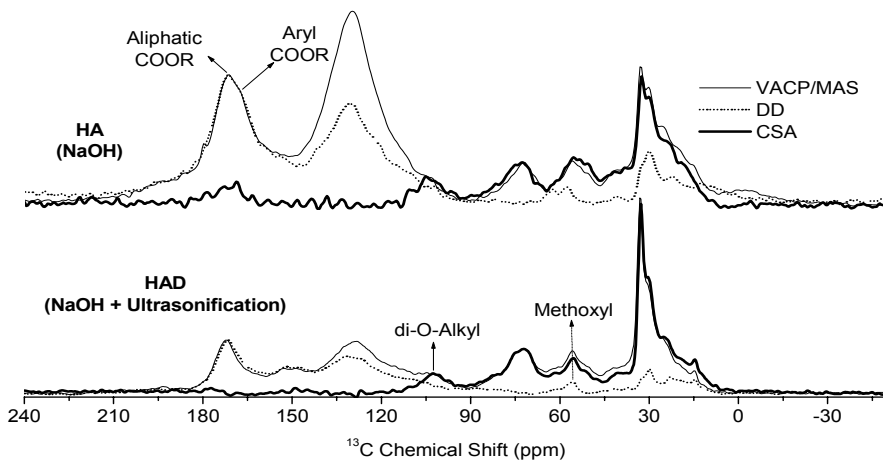


Figure 1. Full VACP spectra (thin line) of humic acids from an Amazonian soil and the corresponding CSA (thick line) and DD spectra (short dot line).

possible aggregating compounds, such as long-chain fatty acids (the 33 ppm signal associated with the aliphatic carboxyl groups at 172 ppm).

The first Principal Component (PC1) accounted for 78% of the total variance and is characterised (Figure 2, right) by positive loadings for crystalline poly-methylene structures (33 ppm) and smaller positive loadings for terminal methyl (15 ppm) and aliphatic carboxyl (175 ppm). On the other hand this PC presents negative loadings for pyrogenic carbon (aryl – 129 ppm and aromatic carboxyl-168 ppm) and ligno-cellulosic residues (153, 105, 73 and 55 ppm).

The scores for the PC1 (Figure 2, left) were greater for the samples extracted with the H-bond breakers (Urea and DMSO), and also for the samples submitted to ultrasonication. This indicates that the mechanical dispersion aided the solvent systems in cleaving H-bonds, and especially the penetrating solvent (DMSO) which facilitated the extraction of a humic material closely associated with the soil mineral matrix. The small scores for PC1 for the Hu, HA and coarse char samples indicate that the residual humin (insoluble in the solvent systems used) is similar to the coarse char (rich in pyrogenic carbon and ligno-cellulosic material). The second PC (13% of the total variance) only differentiated samples from the different soils (1, 2 or 3).

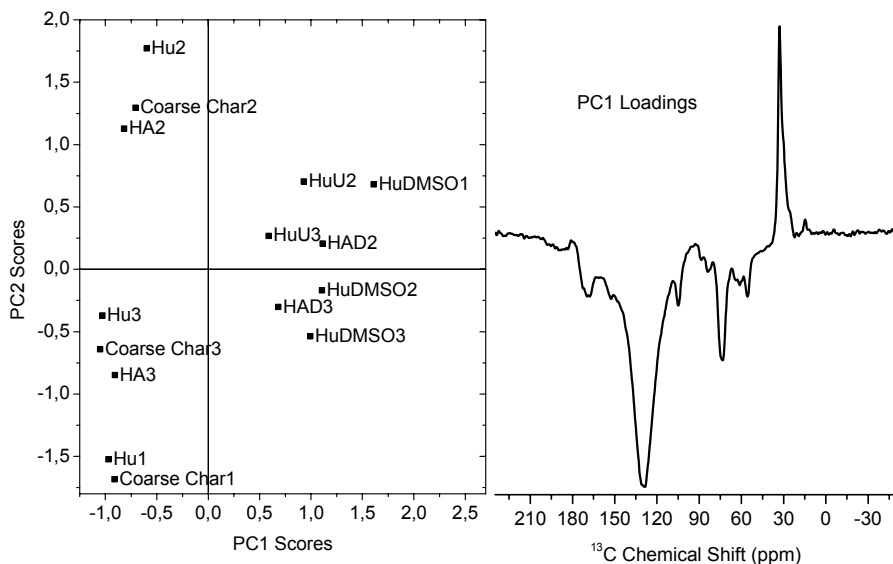


Figure 2. PCA loadings (right) and scores (left) from full VACP spectra.

4. CONCLUSIONS

The use of extraction systems that promote cleavage of H-bonds facilitated the extraction of additional humic substances that are humin in the classical definition. This material is more hydrophobic than the fractions obtained by the classical alkali solution method. The additional fractions contained significant amounts of long-chain fatty acids, mainly with crystalline poly-methylene structures, indicating that these compounds are important for the soil aggregation. The residual insoluble humin is probably colloidal charcoal and derivatives of vegetable debris (lignin and cellulose).

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