



Humic Acids and Water Extractable Organic Matter (WEOM) along a deep soil profile

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Introduction

The evolution of soil organic matter (SOM), transformation and synthesis processes of humic substance (HS), the origin and the fate of dissolved organic matter are important and unsolved questions for most soil scientists. The main objective of this work is to evaluate some physico - chemical properties of humic acids (HAs) and WEOM isolated from the different horizons of a deep soil profile of a typical Mediterranean area by means of spectroscopic characterization.

Materials and Methods

The HAs and the Dissolved Organic Matter (DOM) were extracted from each horizon of a soil profile located in "Monte Pietroso", a site of the National Park "Alta Murgia" in Puglia Region, Italy. The depth of the profile was about 200 cm, developed on a calcareous material ("Calcare di Bari") and it was classified, according to the Soil Taxonomy (Soil Survey Staff) as an Alfisol with xeric moisture regime. The eight horizons [Ap1-Ap2-Ab1-Ab2-Bt1-2B-2Bt2-2B/C], recognised in field by means of chromatically and morphologically differences, were collected in October 2002. HAs were isolated from each horizon according to conventional procedures and characterized by physico-chemical techniques, such as Fourier transform infrared (FT-IR) and fluorescence spectroscopies. Infrared spectra were recorded on pellets obtained by pressing under reduced pressure a mixture of 1 mg of HA and 400 mg of dried KBr, using a Nicolet 5PC FT-IR spectrophotometer and an Omnic 1.2 software. Three dimensional and conventional fluorescence spectra [respectively, in excitation/emission matrix (EEM) mode and in emission, excitation and synchronous-scan modes]; were

recorded on aqueous HA solutions at a concentration of 50 mg L⁻¹ adjusted to pH 8, by using the Noesy 2.4 software. WEOM was extracted by gentle stirring for about 10 min with 10 mM CaCl₂ solution at room temperature, followed by centrifugation at 4000 rpm for 10 min and filtration through a 0.4 μm pore polycarbonate filter. Then, solutions were acidified to pH 2 with 2N HCl prior to further analyses. Each extracted WEOM solution was analysed for dissolved organic carbon (WEOC) concentration and spectroscopic parameters. Numerous additional parameters are derivable from spectroscopic analyses. In this study are reported: 1) Aromaticity Index of the WEOM, measured indirectly from the UV absorptivity at 254 nm, expressed as L mg⁻¹ m⁻¹; 2) the emission spectrum (obtained exciting the sample at 254 nm); 3) the Humification Index (HIX), calculated from the emission spectrum; and, 4) the Fluorescence efficiency (F_{eff}), which results from the ratio between the maximum fluorescence intensity (F_{max}) of each emission spectrum and the relative UV absorption at 254 nm (F_{max}/Abs). Moreover, three dimensional spectra, excitation/emission matrix (EEM) mode were recorded on WEOM extracts.

Results

The main features and variation of the FT-IR spectra of the HA along the soil profile are: a) an absorption band at 2920 cm⁻¹ (aliphatic C-H stretch), whose intensity decrease with the increase of the depth of soil profile; b) a peak around 1715 cm⁻¹ (various C=O groups, mainly COOH vibrations) which shows a relative increase of intensity from Ap1 (0-4 cm) to Ab2 (60-85 cm) horizon; then, it assumes an opposite trend; c) a variable peak at 1620 cm⁻¹ (C=C aromatic vibration) observed in the Ap1, Ap2, Ab1 e Ab2 horizons; then, in deeper horizons it shows a constant decrease; and d) a band located around 1040 cm⁻¹ (C-O stretch of polysaccharide-like substances) which appears rather weak in Ap1, it disappears in Ap2, Ab1 and Ab2 horizons, but progressively increases in intensity in the lowest part of soil profile (from Bt1 to 2B/C). In general, these results confirm the presence of significant structural differences between the HAs of the upper part of soil profile (0-85 cm) with respect to the HAs of the lower one (85-195 cm). The former are more aliphatic with a relative abundance of carboxylic groups, the latter are more aromatic and show a marked signal ascribed to polysaccharidic structures. Fluorescence Intensity (FI) values measured on the main EEM peaks of HA samples decrease along the soil profile. The WEOM isolated from the eight horizons was characterized valuating the aromaticity, the HIX and F_{eff}. The aromaticity of the WEOM isolated from the eight horizons is apparently very high in the top horizon of the soil profile (Ap) but it decreases dramatically towards the lower ones. In general, this could be simply ascribed to the inputs of fresh organic residues onto the soil surface and to its active and rapid transformation processes which tend to accumulate all possible types of biomolecules in

the top portion of the soil. Further, both plants and microorganisms produce a wide number of highly aromatic compounds which are rapidly released into the soil liquid phase. In the following horizons, the aromaticity of the WEOM appear approximately half of the initial value. It decreases slightly towards the central portion of the profile but it increases again towards the lower horizons. The lowest value is reached in the WEOM isolated from the Ab2 horizon whereas the highest one is reached in 2B. Emission spectra of the various soil extracts present a large variability of features both for the relative fluorescence intensities and for the maximum wavelengths. The WEOM extract isolated from the Ap1 horizon shows the highest fluorescence intensity and also the highest maximum wavelength among all samples. Here, the emission spectra have been mainly used to measure and derive humification indexes (Zsolnay, 1999) and fluorescence efficiency of the WEOM along the profile. Molecular and functional consideration on the dissolved material is not mentioned herein. The Humification Index presents a trend similar to the aromaticity one, especially for the initial portion of the profile. In fact, the WEOM isolated from the first two horizons seems apparently markedly more humified than the WEOM from the lower profile. The HIX shows then a uniform but much slighter decrease which the only exception recorded for the DOM isolated from the Bt1 horizon. The Fluorescence Efficiency (Feff) describes simply the relationship existing between the maximum fluorescence intensity of each spectrum and the UV absorption at the excitation wavelength. This last parameter is considered to be proportional to the quantum efficiency of the fluorophores (Zsolnay, 2003). It is rather interesting to see that, beside the WEOM samples of the first top horizons, the molecular efficiency of WEOM tends to be very high in the isolates of the lower horizons of the profile. This is in agreement with the theoretical consideration that the dissolved organic matter is mobile throughout the soil profile, that specific fractions of WEOM are chemically and/or physically retained onto soil particles of specific horizons (Kalbitz, 2001) and, finally, that selected molecules with typical structural and functional properties are rather mobile and able to reach very remote and distinct portions of the soil profile. This is confirmed by the EEM data. Generally speaking, three different fluorophores, named a, b, and c, are observed in the EEM spectra, with varying fluorescence intensities and not necessarily occurring in all horizons.

Conclusion

Results are clearly consistent with the theoretical wide heterogeneity of soil organic matter and particularly the dissolved fraction. The high sensitivity of simple spectroscopic approaches may provide with additional detailed information about nature of organic matter in natural and partly anthropogenic soils.

References

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