

Wildfire-Induced Changes in the Quantity and Quality of Humic Material Associated to the Mineral Phase

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Abstract The analysis of the humic material in the particle-size fractions of fire-affected (FA) and fire-unaffected (FU) Cambisols and Leptosols from the Sierra de Aznalcóllar confirms that already shortly after a fire, degraded charred organic matter can interact strongly with the mineral phase. Applying solid-state ^{13}C NMR spectroscopy, we identified pyrogenic organic matter in all particle-size separates, although the clearest evidence for its presence was obtained for the sand fraction. Difference spectra indicated that in the sand fractions of the FA soils, the *O*-alkyl C content decreased relative to that of the FU soil. This observation may be explained by the fact that in general, this fraction contains a considerable amount of particulate organic material with low humification degree and high accessibility for microorganisms. After the fire event, such material entering the soil as litter was quickly degraded, whereas the more resistant pyrogenic organic matter accumulated. Some of the latter must have suffered further disintegration due to weathering and partly degradation by microorganisms, leading to the production of smaller particles which can interact with the minerals of the small fractions. This interaction is likely to contribute to their stabilization and may explain the observation that in several soils with ancient fire history, charcoal residues were mainly found in the silt and clay fractions.

Keywords NMR spectroscopy • Charcoal • Vegetation fire • Forest soil • SOM stabilization • Physical fractionation

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Introduction

After wildfires, charcoals together with charred plant residues are suddenly introduced into the soil system. The charring process is accompanied by drastic chemical alterations of the litter material, which are manifested in the transfer of biologically available structures such as carbohydrates, proteins, and lipids into aromatic polymers. Thus, the input of charred residues into soils is expected to have a major impact on the quality and quantity of their humic material but also on the processes involved in humic substance formation.

Recent studies indicated that charcoal is biochemically less recalcitrant than commonly assumed (Hamer et al. 2004). Determining mean residence times of the charcoal fraction in fire-affected soils by means of respirometry indicated that they are only slightly longer than those observed for fire-unaffected humic material (Knicker et al. 2012). Other studies revealed the formation of carboxylic groups during the microbial transformation of charcoal (Brodowski et al. 2005). Such groups can increase the solubility of charred residues in the soil solution but can also facilitate their adsorption onto the mineral phase. Considering that this interaction presents an important stabilization pathway for fire-unaffected humic material, this mechanism is also discussed to contribute to the sequestration of charred residues in soils.

With this in mind, the goal of the present study was to obtain more insights on the impact of the incorporation of charred residues on the nature of humic material associated with the mineral phase. Therefore, we compared the composition of the latter in different particle-size fractions obtained from fire-affected and fire-unaffected soils of the Sierra de Aznalcóllar, southern Spain, by means of elemental analysis, solid-state NMR spectroscopy and pyrolysis GC-MS.

Material and Methods

The fine earth (<2 mm) analyzed in the present study derived from the A horizons of fire-affected (FA) and fire-unaffected (FU) Cambisols and Leptosols from the Sierra de Aznalcóllar (southern Spain). For comparison, plant residues and charred pieces found in the skeleton of the soils were isolated and separately analyzed. Additionally, the litter layer from site FA was sampled. It contained fresh material produced during the recovery of the vegetation after the fire event and pieces of partly degraded and charred plant residues. The fine earth was fractionated further into the sand (2 mm to 63 μm) and coarse silt (63–20 μm) by wet sieving. The finer fractions were separated into medium silt (20–6 μm), fine silt (6–2 μm), and clay (<2 μm).

Total carbon (CT) and nitrogen (NT) were determined by dry combustion (975 °C). The chemical composition was examined by pyrolysis using a Curie Point Pyrolyzer connected in tandem with a GC-MS, and by solid-state ^{13}C and ^{15}N NMR spectroscopy of the hydrofluoric-acid-treated samples using the cross polarization magic angle-spinning technique.

Results

Comparison of the chemical composition of the charred and fire-unaffected plant residues supported that wildfires lead to a considerable increase of aromatic structures and a decrease of *O*-alkyl and peptide components. The degree of those alterations, however, clearly depends upon the strength of the charring. The solid-state ^{13}C NMR spectrum of the litter layer of the FA site, on the other hand, showed no indication for the presence of higher amounts of charred plant residues, possibly because the predominant input material during the recovery time after the fire was fresh litter.

Elemental analysis of the humic material of the bulk soils indicated an enrichment of organic C and N caused by the fire event. According to the solid-state ^{13}C and ^{15}N NMR spectra, this was mainly due to the input of aromatic and heterocyclic structures. Application of pyrolysis GC-MS revealed the disappearance of pyrolysis products that derive mainly from polysaccharide and polyphenol precursors in the sample from FA, which can be interpreted with the increase of charred “non-pyrolyzable” refractory carbon. Comparable observations were made for the pyrograms of the particle-size fractions.

Examining the composition of organic matter associated with the different particle-size separates of the FU soils by solid-state ^{13}C NMR spectroscopy confirmed a depletion of *O*-alkyl C and an accumulation of alkyl C with decreasing particle size (Fig. 1). This can be related to the preferential accumulation of organic matter with a higher humification degree in the smaller size fractions. The amount of aromatic structures were found to increase from the sand-size to the medium-silt-size fraction (Fig. 1), which is commonly explained by the relative preservation of lignin degradation products. However, these compounds lose their importance in the fine silt and clay fractions. Inspection of the solid-state ^{15}N NMR spectra demonstrated that in the FU soils, almost all N is bound in amides and considering the decrease of the C/N ratio with decreasing particle size allows the conclusion that accumulation of peptide structures is mainly responsible for the relative increase of alkyl C in the fine fractions.

The solid-state ^{13}C NMR spectra of the particle-size fractions of the FA soils reveal that already shortly after the fire, charcoal residues are interacting with the mineral phase. Although to a different extent, all fractions were affected by the charcoal input.

For further analysis, the C-content-weighted intensity distribution of the solid-state ^{13}C NMR spectra of the particle-size fractions from one fire-unaffected site was subtracted from one fire-affected site. With this approach, we intended to obtain some insights into the alteration of the chemical composition of the humic material of the mineral fractions caused by the fire.

For all separates, the pattern of the difference spectra resembles that observed for charred organic matter, although the aromatic C to *O*-alkyl C ratio indicated differences in their charring degree. While the fractions $<63\ \mu\text{m}$ still revealed an accumulation of *O*-alkyl C, the difference spectrum of the sand-size separate showed a clear depletion in this chemical shift region and the highest aromatic

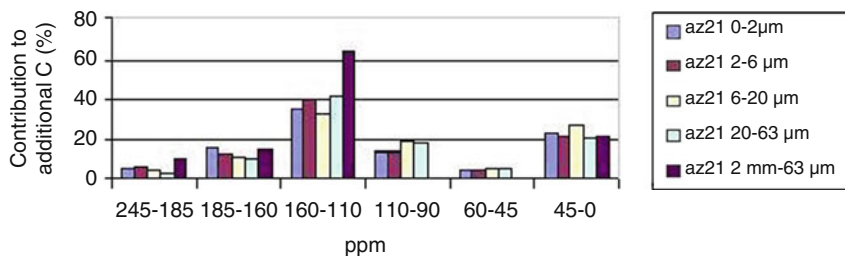


Fig. 1 Relative distribution of C compound classes in the additional C accumulated in the particle size fractions of a fire-affected soil from the Sierra de Aznalcóllar

C content. Accordingly, the solid-state ^{15}N NMR spectrum of the sand-size fraction from FA showed the highest amount of pyrrole-type compounds. In the FU soils, the sand-size fraction is considered to comprise organic material easily available to microbial decay. In the FA soils, the source of organic matter input contains charred material, exhibiting a lower microbial degradability. Thus, during the time after the fire event, accessible carbohydrates and peptides may have been preferentially degraded, whereas aromatic structures of the char residues accumulated. However, disintegration of the charred particles due to, but also their partly degradation, may be responsible for the production of smaller particles and thus for the increase of aromatic C intensity, as it was observed in the spectra of the smaller particle-size fractions. Increasing the recovery time after a fire event will also prolong the time for weathering and degradation, and the bigger charcoal particles presently recovered in the sand fraction may allocate the charred residues into the finer fractions. The fact that in our soil the period between sampling and fire event was only up to 5 years but exceed decades in some Australian soils (Skjemstad et al. 1993) may be one reason why in our study the major part of charred residues were identified in the coarse fraction, whereas in the Australian soils, most of this material was recovered with the fine fractions.

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