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On the structural factors of soil humic matter related to soil water repellence in fire-affected soils

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In order to elucidate the impact of forest fires on physical and chemical properties of the soils as well as on the chemical composition of the soil organic matter, samples from two Mediterranean soils with contrasted characteristics and vegetation (O horizon, Lithic Leptosols under Quercus ilex and Pinus pinaster) and one agricultural soil (Ap horizon, Luvisol) were heated at 350 $^{\circ}$ C in laboratory conditions for three successive steps up to 600 s.

The C- and N-depletion in the course of the heating showed small changes up to an oxidation time of 300 s. On the other side, and after 600 s, considerable C-losses (between 21% in the Luvisol and 50% in the Leptosols) were observed. The relatively low N-depletion ca. 4% (Luvisol) and 21% (Leptosol under pine) suggested preferential loss of C and the subsequent relative enrichment of nitrogen.

Paralleling the progressive depletion of organic matter, the Leptosols showed a significant increase of both pH and electrical conductivity. The former change paralleled the rapid loss of carboxyl groups, whereas the latter point to the relative enrichment of ash with a bearing on the concentration of inorganic ions, which could be considered a positive effect for the post-fire vegetation.

The quantitative and qualitative analyses by solid-state 13C NMR spectra of the humic fractions in the samples subjected to successive heating times indicate significant concentration of aromatic structures newly-formed in the course of the dehydration and cyclization of carbohydrates (accumulation of black carbon-type polycyclic aromatic structures), and probably lipids and peptides. The early decarboxylation, in addition to the depletion of O-alkyl hydrophilic constituents and further accumulation of secondary aromatic structures resulted in the dramatic increase in the soil water drop penetration time. It was confirmed that this enhancement of the soil hydrophobicity is not related to an increased concentration of soil free lipid, but is explained by changes in the surface properties of the macromolecular soil humic fractions. It is worthy to mention that whereas in mineral soils a considerable chemical alteration of the organic matter occurred only after a heating time >300 s, in the case of organic soils large transformations occur after 90 s. This could suggest the extent to which the soil mineral phase protects the organic matter during the fire event. The composition of the soil lipid assemblages showed very significant qualitative and quantitative changes: the maxima of the alkyl homologous series shifted towards short-chain compounds (indicating thermal breakdown of long-chain alkyl compounds). Additional progressive changes of the Carbon Preference Indexes (relative abundance of odd- versus even-C numbered alkyl molecules, which tended to one) were observed such as the progressive smoothing of the biogenic signature of the alkyl series, probably simultaneous to a re-compartmentalization of lipid species within soil microaggregates.