

## **PBC-14: Molecular level descriptors of the effect of fire on soils under pine forest in continental Mediterranean soils**

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The relatively frequent occurrence of wildfires in Mediterranean ecosystems is favoured by hot summer temperatures in addition to the historical reforestation with pyrophytic forest species such as most types of rapid growing conifers used in the second half of the past century. Concerning soil organic matter, it has been demonstrated that fire leads to progressive decarboxylation, dehydration and dealkylation of the humic and fulvic acids which, in turn, lead to insoluble polyaromatic macromolecular substances (humin-like). This material has been generically referred to as black carbon, a recalcitrant soil fraction which is considered of large interest by their possible effect in the biogeochemical balance with a significant impact on the global change through the soil C sequestration processes.

Although fire is considered to be one out of the abiotic factors with most significant bearing on the organic matter characteristics, assessing the occurrence of forest fires in the past is not a trivial problem since several studies have shown that fire-induced changes in soil properties cannot be easily distinguished from the effects of the biochemical humification process despite the latter may take hundred of years in undisturbed soils. In particular no sufficient information is currently available on important issues such as: **a)** the analytical descriptors betraying the effects of fires in soils with unknown history of external perturbations, **b)** those molecular features of black carbon and charred biomass that could be used to quantify these soil components and **c)** the organic matter descriptors most suitable to monitor the intensity-dependant effects of the different types of wildfires.

In this work a series soil organic matter fractions (lipids and humic acids) from two pine forests and from the corresponding neighbor plots affected by high- and medium-intensity wildfires (in the latter case fire mainly affected forest canopy) were characterized aiming to select significant parameters responsive for the effect of fire on the soil. In the case of humic acids visible, infrared and <sup>13</sup>C NMR spectroscopy (Bloch-decay and dipolar dephasing), in addition to degradation methods (perborate degradation and Curie-point pyrolysis) were used, whereas the soil lipid fraction was methylated and studied directly by gas chromatography-mass spectrometry.

Microscopic examination of particulate soil fractions isolated by flotation in dense liquids suggests that qualitative and quantitative changes after medium-intensity fire could mainly be attributed to the fall of charred plant material from the forest canopy, whereas the

high intensity fire turn most of the plant biomass into black carbon-like material and ash, and leads to severe transformation of the preexisting organic matter.

Several of the variables determined in the humic acid fraction could be considered as possible descriptors of wildfire impact. This was mainly the case with the yield of benzenecarboxylic acids after perborate degradation, which increased to different extent depending on the intensity of the wildfire (x3 in the most intense forest fire), whereas the amount of fatty acids released after degradation increased only in the humic acids from the soil under the forest affected by the medium-intensity fire. The  $^{13}\text{C}$  NMR spectra confirm the substantial increase in the total amount of aromatic structures, but other spectral characteristics such as the intensity of the infrared and NMR bands produced by oxygen-containing functional groups showed significant variations in terms of the type of fire (e.g., some oxidation may occur in medium-intensity fires). On the other hand, there was a series of molecular descriptors showing progressive trends hence being more suitable for the quantitative assessment of the fire intensity. For instance, there was a highly significant increase in the N content of the humic acids in terms of the effect of fire. The atomic H/C ratio (elemental analysis) showed a decrease in the postfire soils, to an extent depending on the intensity of the wildfire, as correspond to the above-indicated enhancement of the aromatic domain. The optical density of the humic acid paralleled the above patterns and reinforces the conclusion about removal (or transformation) of the whole aliphatic moieties.

Compounds behaving as biomarkers of the contribution of the fungal metabolism to the humic acid synthesis, such as the perylenequinonic pigment recognized by intense valleys at 455, 530, 570 and 665 nm in the second derivative spectra of the humic acids from soils under burnt forest were also significantly depleted (a phenomenon that could be tentatively attributed to a reductive insolubilization of humic acid fraction leading to the accumulation of these polynuclear pigments in the alkali-insoluble humin-like fractions).

Results from Curie-point analytical pyrolysis indicated that methoxyphenols are the pyrolytic products most responsive to fires' effects whereas the amount of fatty acids behaves as in the perborate digests: they increased to some extent after the medium-intensity fire. This conspicuous behavior of the fatty acid associated to humic acid structure could be pointing out to translocation and further fixation of hydrophobic compounds.

There was an also very significant change in the molecular assemblages of soil lipids extracted from soil with petroleum ether and analyzed by gas chromatography. The alkane concentration increased after both types of fires. In the soil subjected to the most intense fire there was depletion in the relative amounts of monoterpenes, sesquiterpenes and diterpenes and increases in the relative amounts or aromatic diterpenoid hydrocarbons. On the other hand, in soil where fire was less intense and mainly affected forest canopy there was a increase in the relative proportion of diterpene hydrocarbons.