

PSB-18: Tentatively quantifying fire impact, organic carbon balance and thermal structural rearrangements by ^{13}C CPMAS NMR of whole soil samples from Continental Mediterranean forests

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Soils from ten Mediterranean pine and oak forests were studied by ^{13}C CPMAS NMR by comparing samples from neighbouring ecosystems affected or not by wildfires. Sample sites differ in fire intensity, duration and propagation models ranging from high intensity fires (in dense pine forest on flat semiarid site) to medium-intensity fires (where most effects on soil organic matter are tentatively attributed to allochthonous C forms from charred litter after a fire event affecting mainly forest canopy).

The soils (mainly Cambisols and Umbrisols) were thoroughly characterized by standard agrobiological analyses (C, N, macro- and microelements and laboratory incubation experiments) and detailed quantification of the humus fractions including lipids, particulate fractions, extractable humic substances and different types of humin.

The aim of the present study was: i) to estimate the balance for several C-types as seen in the ^{13}C NMR spectra (carbonyl, aromatic, *O*-alkyl and alkyl and their subranges) taking into account the C concentration in undisturbed and fire-affected soils, in an attempt to assess how changes in different structures could be related with fire type, ii) to make a tentative classification of forest fires according to their selective impact on the different C-types, and iii) to calculate an impact index in the whole soil organic matter considering the statistical dissimilarity between the spectral profile from undisturbed and fire-affected soils.

In order to distinguish recalcitrant structures and—as negative signals—any positive balance of soil C forms from allochthonous organic matter and/or thermal conversion of e.g., aliphatic structures into aromatic ones, subtraction spectra were obtained from paired (undisturbed minus fire-affected) soil samples after full-scale normalization based on total C content. Correspondence analysis and Euclidean distances between soils defined by variables consisting of relative fire-induced changes in eight C-types calculated from signal area values were also considered. The results pointed to an unexpectedly high variety in the transformation patterns of the organic matter depending on the intensity and type of wildfire. In the soil showing the greatest transformation as regards its corresponding control (*Pinus halepensis* forest on Calcaric Cambisol in Central Spain) it was evident that fire caused intense depletion of aliphatic structures (0–110 ppm) and carbonyl/amino groups (172 ppm signal), with the concomitant increase in aromatic/unsaturated constituents. That evolution is explained mainly from selective depletion in all C-types, the ratios between them suggesting that alkyl structures were found to be comparatively more recalcitrant than *O*-alkyl ones.

After a medium-intensity fire (mountain pine forest) a considerable enrichment in aromatic C forms was found to some extent higher than that calculated from the negligible variation in the total

soil C (69 and 64 g kg⁻¹ in undisturbed and fire-affected soil, respectively): this secondary C forms are interpreted as from the conversion of aliphatic structures into aromatic ones in addition to a compensating effect of the fall of burning litter.

In the extreme situation according to fires impact on soil (Dystric Xerochrept under *Quercus rotundifolia* forest) the spectra clearly showed enrichment in lignin not explained as an effect concomitant to the depletion of comparatively thermolabile compounds. The spectra suggested non-altered methoxyl substitution patterns in lignin, fairly intact alkyl- and *O*-alkyl structures and no effective decarboxylation. These patterns could define a signature for low self-combustibility of evergreen oak leaves incorporating into soil as not totally charred litter.

Once the above conditions are fixed to define a virtual gradient for the progressive thermal impact estimated as the extent to which the NMR profile has changed in the post fire soil, a series of collateral, intermediate situations were recognized: the NMR spectrum of a Dystric Xerochrept under pine forest suggested a scenario in which most of the organic matter was allochthonous material not only consisting of black-carbon particles but also of aliphatic and N- and O-containing aromatic structures indicating thermal reworking of plant biomacromolecules. In fact, after the passage of the fire this soil showed enhanced signal intensity in the carbonyl/amide and alkyl (0–45 ppm) spectral regions and a defined methoxyl/ α -amino peak (56 ppm). The striking enhancement of the alkyl/*O*-alkyl ratio after fire suggests accumulation and/or fixation of litter-derived water repellent substances, which coincides with the hydrophobic properties observed in the post-fire soil. Nevertheless, considering that fire increased both C and N levels in this soil, the contribution of melanoidins or other N-containing structures in the 0–45 ppm spectral region (and probably in the 56 and 175 ppm signals) should not be ruled out.

A different situation is observed in a Cambisol under *Pinus pinaster* forest, where not only the whole aromatic domain increased but also the ratios between O- or N-substituted/H-substituted aromatic Cs and the alkyl/*O*-alkyl ratio. This is interpreted as an intense modification in the stoichiometry of the original plant biomacromolecules; the C and N balances suggest prevalence of rearrangement processes of autochthonous organic matter with incorporation of thermally altered N forms into the surviving organic matter.

In conclusion the NMR profiles have led to discriminate a series of wildfire-induced patterns at first sight based on a common background irrespective of soil and forest type (aromatic enhancement, accumulation of O- or N-linked aromatic structures, systematically more recalcitrant than the *O*-alkyl (mainly carbohydrate) moiety. This common pattern overlaps with specific changes clearly distinguishing the different fire scenarios. These local differences include features such as the relative alkyl enhancement in soils developing hydrophobic properties, the possible oxidation and/or accumulation of melanoidins in heavily rearranged pyromorphic humus, external inputs of slightly altered lignin and carbohydrate, or the unspecific mineralization leading to black carbon-like residue. It is presumed that the above described variety of thermal rearrangement processes are perhaps causally associated with the specific soil physical and chemical properties (including N balance) observed in the post-fire soils.