

# Tentatively quantifying fire impact, organic carbon balance and thermal structural rearrangements by $^{13}\text{C}$ CPMAS NMR of whole soil samples from Continental Mediterranean forests



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## Introduction

Whole soil samples from Mediterranean pine and oak forests were studied by  $^{13}\text{C}$ CPMAS NMR by comparing neighbouring ecosystems affected or not by wildfires. Sample sites differ in fire intensity, duration and propagation models, ranging from high intensity fires (dense pine forest on semiarid site) to medium-intensity fires (where most effects on soil are attributed to inputs 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.

The aim of the present study is manifold: i) to estimate the balance (depletion vs. net increases) for several C-types, ii) to make a tentative classification of forest fires according to their relative changes in the different C-types, and iii) to calculate a comprehensive index for the impact of fire on the whole soil organic matter considering the statistical dissimilarity between the spectral profile from undisturbed and fire-affected soils.

## Results

High variety in the transformation patterns of the organic matter depending on the intensity and type of wildfire were found. In the soil showing the greatest transformation as regards its corresponding control (*Pinus halepensis* forest on Calcic Cambisol in Central Spain, **Ph**; Fig. 1) it was evident that fire caused intense depletion of aliphatic structures (0–110 ppm) and carbonyl/amino groups (172 ppm signal), with 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, **Pp**) an enrichment in aromatic C was found to some extent higher than that calculated from the negligible variation in total soil C (Table 1) between undisturbed and fire-affected soil: this secondary C forms are interpreted as a conversion of aliphatic structures into aromatic ones in addition to the effect of the fall of burning litter.

In the extreme situation according to fires impact on soil (Dystric Xerochrept under *Quercus rotundifolia* forest) there was enrichment in lignin not explained as an effect concomitant to the depletion of 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 dead, not extensively charred litter.

A series of 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 from thermal reworking of biomacromolecules.

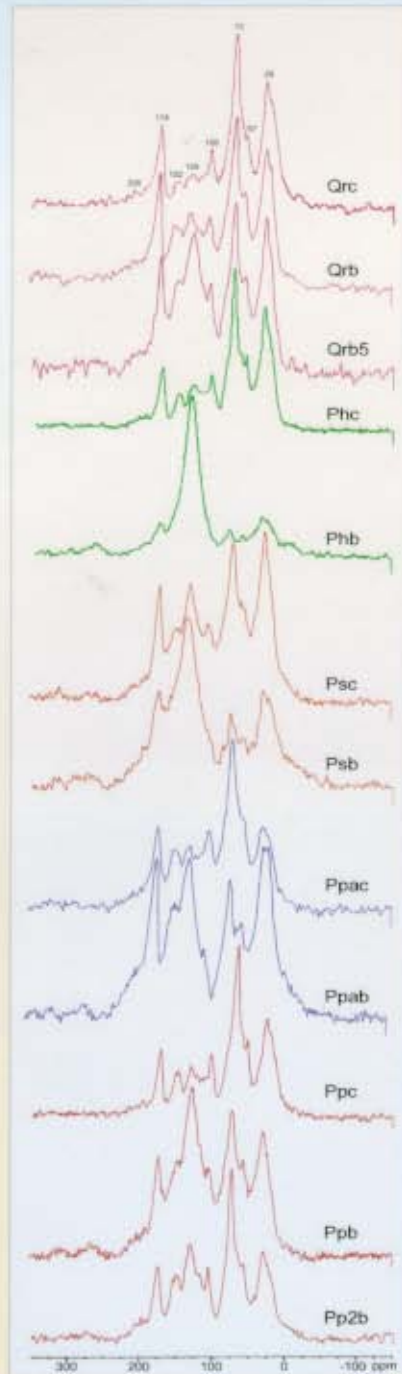


Figure 1. CPMAS  $^{13}\text{C}$  NMR spectra of whole soil samples from unburnt and burnt Mediterranean forests

Table 1. Some chemical characteristics and  $^{13}\text{C}$  NMR integration values for the main spectral ranges in samples from unburnt and burnt Mediterranean forests

| Soil (Forest)  | pH  | C (%) | N (%) | Total C |      | Aromatic C |      | Alkyl C |      | O-alkyl C |      | N-alkyl C |  |
|----------------|-----|-------|-------|---------|------|------------|------|---------|------|-----------|------|-----------|--|
|                |     |       |       | g/kg    | g/kg | g/kg       | g/kg | g/kg    | g/kg | g/kg      | g/kg |           |  |
| Qrc (Quercus)  | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Qrb (Quercus)  | 4.2 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Qrb5 (Quercus) | 4.2 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Phc (Pinus)    | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Phb (Pinus)    | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Psc (Pinus)    | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Psb (Pinus)    | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Ppac (Pinus)   | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Ppab (Pinus)   | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Ppc (Pinus)    | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Ppb (Pinus)    | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |
| Pp2b (Pinus)   | 4.1 | 38.0  | 0.8   | 12      | 3    | 4          | 15   | 15      | 24   | 5         | 25   |           |  |

In fact, after the passage of the fire (**Ppab**), this soil showed enhanced carbonyl/amide and alkyl (0–45 ppm) signals and a defined methoxyl/ $\alpha$ -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. 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 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 sylvestris* forest (**Ps**), 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.

## Conclusions

The NMR profiles have led to discriminate a series of wildfire-induced patterns 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 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 residues. It is presumed that the above 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.