Characteristic Alterations of Quantity and Quality of Humic Substances in Forest Soils Caused by Wild-Fires

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1. INTRODUCTION

Humic substances play an essential role in active environmental compartments in which biogeochemical processes have a direct impact on primary production and biodiversity. Both quality and quantity of the organic matter with special reference to N-bearing fractions in forest soils is known to be severely affected by wild fires. However, reports on fire-induced effects on humic substances often lead to divergent conclusions which may depend on local factors and make it difficult to postulate a generalized model about the lasting effects of fires on HS. In fact, recent studies have paid special emphasis in establishing the opposed effects of the high-intensity wildfires (leading to C mineralization in litter and surface organic horizons) and the prescribed burnings or cold fires where most of the pre-existing soil organic C is preserved, and soil incorporates important inputs from charred material. Therefore, to elucidate the impact of those factors on humic substance composition and stability, various fire-affected and control soils from Mediterranean forests were analyzed.

MATERIALS AND METHODS

Soil samples derived from areas around Madrid (Central Spain) and Sevilla (Southern Spain) and were characterised by elemental analysis and solid-state and ¹⁵N NMR spectroscopies. Char contents were determined by difference and compared with data from chemical oxidation methods. Short-term
effects were assessed from samples taken up to 2 years after the fire, whereas a long-term alteration was analyzed with soil samples taken 5 to 20 years after burning, in both cases comparing the samples with the corresponding controls.

3. RESULTS AND DISCUSSION

The present study showed that the short-term effect of the forest fires were highly variable depending on numerous factors such as fire intensity and duration, amount and flammability of the vegetation and the litter. The effects observed ranged from a dramatic loss of humic material in the topsoil to an increase of humus by incorporation of necromass fallen on the ground which is composed of dry leaves, but also charred plant remains. Whereas the fire-affected soils showed no common pattern in terms of the amount of additional carbon \( (C_{\text{add}}) \), in all the sites studied the fire enhanced the relative amounts of aromatic C.

The lowest intensity wildfire resulted in the highest aromatic enrichment factor, \( EF_{\text{aromatic C}} \) suggesting the highest local accumulation of char. The respective \( C_{\text{add}} \) disclosed an \( EF_{\text{aromatic C}} \)-to-\( EF_{\text{alkyl C}} \) ratio \( (B_{\text{char}}) \) of \( \approx 1 \) supporting a low charring degree. Extensive combustion and volatilization at higher fire intensities resulted in a decrease of \( EF_{\text{aromatic C}} \) and an increase of \( B_{\text{char}} \). These trends are in good agreement with fire intensity and forest fuel combustibility in the various sites and therefore, these indices could be considered quite responsive for the quality and quantity of char input occurring during and after forest fires. Char contents elucidated by the NMR technique were compared to those determined by chemical oxidation methods. No \(^{13}\text{C} \) NMR evidence for substantial inputs from non-charred plant necromass was found for any of the single-burnt soils. The high amounts of carbonyl Cs in \( C_{\text{add}} \) suggested oxidation reactions occurring during or already shortly after the fire. Irrespective whether this was induced by microbial activity or caused by abiotic reactions, the resulting oxidative chemical alterations are likely to increase char availability for microbial attack and thus decrease its long-term refractory nature. The suspicion that black carbon exhibits lower recalcitrance than commonly assumed—mainly in warm humid climates—has already been published \( (1) \). Previous studies demonstrated CO\(_2\) production during microbial degradation of char \( (2) \). On the other hand, the formation of polar carboxyl C structures could also have a side-effect in increasing the stability of charred residues by
enhancing adsorption to the mineral phase in particular to metal oxides (3). On the other hand, a higher carboxylation of charred residues can increase the water solubility of the originally non-polar remains then promoting continuous leaching into deeper horizons that could also add to the progressive removal of pyrogenic SOM in the topsoil. Such a scenario could also explain the relatively high aromatic C proportion of the SOM in the single-burnt B horizon of site P2 and the observation that in spite of high fire activity of ancient times, only weak indications for higher char accumulation could be found in many topsoils. Therefore, although the uppermost horizon are affected by fire to a much higher extent, the suspected translocation of charred remains within the soil (both due to bioturbation processes and to the above-suggested post-fire reactions leading to hydrophylic C fractions) suggests the need of a more detailed analysis of subsoils, for a better understanding of the impact of fire on soil organic matter.

Comparing the single and double-burnt sites, no additional char input was observed for the double-burnt site, possibly because of a more complete combustion of young trees, shrubs and char remains during the second fire. In fact, the high O-alkyl C proportion found in $C_{ads}$ of the double-burnt soil, is best explained by reduced litter degradation.

Considering the N-fraction, the fire resulted in an accumulation of pyrrole-type N-forms, although most of the signal intensity in the respective $^{15}$N NMR spectra is still originating from amide N. The latter either indicates that not all peptide-structures of the necromass were transformed by the fire, or that it could have become stabilized in amide-containing melanoidin-like structures, known to be formed during thermal treatment of carbohydrate and amino acid mixtures. Pyrrole-type N was also identified in solid-state $^{15}$N NMR spectra of other fire-affected soils (4), but remained undetected in solid-state $^{15}$N NMR spectra of humic substances derived from fire-unaffected areas (5, 6) analyzed in our laboratories. This supports that heterocyclic N in soils has a pyrogenic origin rather than being the product of microbial and humification processes. Thus, their identification in SOM by means of solid-state $^{15}$N NMR spectroscopy may be taken as a first unambiguous indication for the presence of pyrogenic humic material, which is difficult to detect solely by solid-state $^{13}$C NMR spectroscopy, due to overlapping of signals derived from char and from biogenic SOM.
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REFERENCES


