SOIL ORGANIC MATTER ALTERATIONS RESULTING FROM **POST-FIRE RESTORATION ACTIONS**

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INTRODUCTION

Burned soils restoration/rehabilitation techniques include tillage, tree logging, reforestation with native or non-native species, and other management. In some cases, restoration may cause additional impacts on soils, producing more severe damages than those caused directly by fire. Triggered soil erosion processes, loss of soil fertility and alterations in the hydrological cycle are among these negative impacts. Analytical pyrolysis (Py-GC/MS) together with graphic interpretation tools like van Krevelen's diagram [1] may be used to shed light on alterations caused by burning and restoration plans to soil organic matter (SOM). The objective of this research is to study fire impacts on SOM in a sandy soil under pine (Pinus pinea) forest affected by a severe fire in August 2012 in Doñana National Park (SW Spain).

METHODS

The impact of fire on SOM was studied in bulk samples and sieved soil fractions (coarse, 1-2 mm, and fine, <0.05 mm) collected from burned adjacent areas before (B) and after restoration practices (BR) (logging and extraction of burned trees). An adjacent unburned (UB) area was used as a control. Bulk soil samples and its fractions were studied by direct Py-GC/MS (500 °C) and the results were interpreted by analyzing van Krevelen diagrams using H/C and O/C atomic ratios calculated from the chemical formulas of compounds as inferred from their mass spectra.

RESULTS AND DISCUSSION

The relative contribution to SOM of the main compound families obtained by analytical pyrolysis is shown in Fig. 1. Conspicuous differences are observed between bulk samples UB and BR with the burnt (B) sample. Compared to the UB and BR sites, the bulk samples from the B site showed lower proportions of lignin methoxyphenols (Lig) and an increase in UAC and PAH. It could be hypothesized that fire produced defunctionalization of methoxyphenols, increasing the proportion of recalcitrant compounds. In all cases, the coarse fraction showed a high content of carbohydrate and lignin derived compounds followed by fatty acids that could be explained by litter (lignocellulosic) inputs to SOM after the fire [2].

Although fine fractions organic composition varied largely from one area to another, it was found generally more altered than in the coarse fractions. In fact, SOM from the UB fine fraction shows a high proportion of alkyl compounds and comparatively lower of carbohydrate- and lignin-derived compounds. In contrast, SOM from B fine fraction did not show a high contribution of alkyl compounds, which may be due in part to the occurrence of thermal cracking of long alkane/alkene chains [3] as seen in Fig. 2. In addition, a high contribution of UAC and PAH was observed in this B fine fraction. Finally, the fine fraction of BR samples showed a high contribution from labile compounds, possibly due to topsoil mixing caused by tilling during rehab actions. The van Krevelen diagram applied to pyrolysis compounds (Fig. 3 and 4) differentiates among main chemical shifts and processes caused by fire and rehab practices to SOM. Among the main processes identified are hydratation (oxidation and hydrogenation), demethylation (oxidation and dehydrogenation) and oxidation-reduction.



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Figure 1. Relative percentage of the main chemical families identified by Py/GC/MS from each scenario. A: alkane/alkene pairs; UAC: unspecific aromatic compounds; P: peptides; Lig: methoxyphenols; FA: fatty acids; S: carbohydrate-derived; N: Nitrogen compounds; PAH: polycyclic aromatic hydrocarbons.



Bulk Coarse Fine Sieve fractions (mm)

Burned and Restored Burned Unburned

Figure 2. a) Short (C9-C23) vs large (C24-C31) alkane/alkene pairs identified by Py/GC/MS from Bulk, coarse (2-1 mm) and fine (<0.05 mm) of each scenario. b) Thermal cracking theoretical scheme.





Figure 3. Probability surface for atomic ratios of pyrolysis compounds (PSAR). For each pyrolyzed sample it represents the probability of including in its composition a number of macromolecular units with the stoichiometry indicated in the x and y axes. AS: Saturated hydrocarbons; AU Unsaturated hydr. & Sterols; UAC: unspecific aromatic compounds; Lig: methoxyphenols; FA: fatty acids; S: carbohydrate-derived; PAH: polycyclic aromatic hydrocarbons

1.32 0.05 0.07 0.09 0.13 0.21 0.15 0.19 0.23 0.11 0.17 Atomic O/C

Figure 4. van Krevelen diagram based in the chemical formula of the pyrolysis compounds as inferred from their mass spectra. Atomic ratios are centroids, mean values of detected compounds.

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