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Variability in the composition of charred litter generated by wildfire in different ecosystems

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ABSTRACT

In most forest ecosystems the burnt material remaining on the soil after wildfire mainly comprises non-woody char derived from the litter layer. Despite the importance of the role of this material in the carbon balance, soil conservation and ecological processes, few studies have examined the properties of this type of charred biomass, which may vary widely in different forest ecosystems and also within burnt areas. In this study, we considered three forest stands (*Pinus nigra*, *Pinus pinaster* and *Eucalyptus globulus*) and two shrubland systems (*Erica arborea* and *Ulex europaeus*), in which some of the properties of the litter differed (amount of fuel, composition and flammability). Changes in the composition of the litter and in chemical and thermal stability indices were studied after wildfires and were related to two visually different levels of soil burn severity (SBS). The methods used included elemental analysis, solid-state ^{13}C CP-MAS NMR spectroscopy, FTIR and DSC-TG.

In all five types of litter, the degree of aromatization increased gradually with increasing SBS, although it was lower than usually found for woody char. The thermal analysis also revealed that the heat released by combustion up to 375 °C decreased with increasing SBS, whereas T50 (the temperature at which 50% of the energy stored in organic matter is released) presents the opposite behaviour. However, the different types of litter were very variable in terms of the amount (*E. arborea* > *E. globulus* > *P. nigra* > *P. pinaster* ≥ *U. europaeus*) and degree of aromatization of the charred material (*E. globulus* > *E. arborea* = *U. europaeus* > *P. pinaster* > *P. nigra*). The differences in composition of the charred litter may be partly due to differences in the heating conditions (determined by the fire regime, initial amount and flammability of the litter). The differences may also be due to differences in chemical degradation of lignin of each plant species during burning. The relationships between thermal properties, elemental composition and chemical-shift regions in the NMR indicate that thermal analysis may be a useful tool for characterizing organic matter properties.

1. Introduction

As a result of predicted climate change scenarios and other human impacts (e.g. encroachment of shrubs after agricultural abandonment and the introduction of flammable monospecific tree plantations), the intensity and frequency of wildfires are expected to increase in many areas (Shakesby, 2011).

The amount and composition of the burnt litter (we used the term litter to refer to the organic soil layers, i.e. fresh litter layer, Oi, fermentation layer, Oe and raw humus layer Oa) vary greatly, depending on soil burn severity, affecting C balance (e.g. Santín et al., 2012), soil run-off erosion (Cerdà and Doerr, 2008; Dlapa et al., 2013; Neris et al., 2013; Vega et al., 2005) and many ecological processes (Bárcenas-Moreno et al., 2013; Vega et al., 2013). Litter is one of the main precursors of soil organic matter (SOM), and many of the properties of mineral soils following wildfire may therefore be directly influenced by the amount and composition of the burnt litter (Bodí et al., 2014; Mastrolonardo et al., 2013).

As the heat increases during wildfire, plant biomass is subjected to chemical transformation involving the formation of aromatic ring structures and the gradual condensation of smaller aromatic units (González-Pérez et al., 2004; Keiluweit et al., 2010). Charred biomass, which is more resistant to microbial decomposition than lignin derived from fresh plant material, acts as an efficient C sink (e.g. Singh et al., 2014). However, this material includes different C forms with varying degrees of aromaticity, such as partly charred plant material, char and

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soot (Schmidt and Noack, 2000). The composition and, therefore, the degradability of these different products are highly variable and depend on heating conditions and the initial composition of the fuel (Hilscher et al., 2009; Kloss et al., 2012; Leifeld, 2007; Soucémarianadin et al., 2013). The degree of aromatization is modified by burn conditions such as temperature and duration of combustion and abundance of O_2. At the temperatures lower than 450 °C usually recorded in wildfires of moderate intensity, the combusted plant material displays a low degree of aromatization/carbonization (Chatterjee et al., 2012; Nocentini et al., 2010). In comparison with pyrolysis (e.g. biochar production), the oxic conditions during combustion also favor the formation of slightly charred biomass including small clusters of condensed aromatic C, which may be degraded by microbial action (Hilscher and Knicker, 2011; Preston and Schmidt, 2006). However, different ecosystems show a high degree of variability in certain factors determining the fire regime and therefore the heating conditions (Miyanishi and Johnson, 2002). Woody fuel and organic layers on the ground are more abundant under forest than under shrubland ecosystems (e.g. Ottmarr et al., 2007; Sikkink et al., 2009), and therefore the temperature is usually higher and the duration of combustion is usually longer in the former (Hungerford et al., 1995; Neary et al., 2005). In addition, the flammability of different types of litter varies greatly due to the presence of certain cations, such as K (which acts as a catalyst), and of resins and terpenes (which increase the energy content and ignitability, e.g. Ormeño et al., 2009). As these factors affect heating temperature, duration of combustion and even the concentrations of gases (Liodakis et al., 2008), they will probably determine the amount and composition of the burnt litter.

The composition of plants may also determine the formation of char and its properties because of variations in the thermal stability of different biopolymers (e.g. much lower for hemicellulose and cellulose than for lignin: Yang et al., 2007). Leaves and grass usually form charred material at a relatively low temperature (~250 °C) because carbohydrates are transformed at this temperature (Keiluweit et al., 2010; Soucémarianadin et al., 2013). This type of fuel usually generates smaller amounts of aromatic and recalcitrant charcoal than woody biomass and thus may be degraded more quickly in soils (Alexis et al., 2010; Nocentini et al., 2010; Wolf et al., 2013). In addition, the higher N content of this type of biomass seems to favor the presence of a higher proportion of N-heteroaromatic compounds derived from protein charring, especially in fires of moderate intensity (Knicker et al., 2008). As a result of the natural variety of fuels present, the amount and composition of charred biomass during wildfire may vary greatly in different ecosystems (McBeath et al., 2013).

In addition to factors determined by the type of vegetation or species, local variations in environmental conditions (soil and vegetation moisture, slope, wind, etc.) lead to high spatial variability in the burn severity, even within a particular area (Keeley, 2009). As a result of these factors, the severity of soil perturbation displays a high degree of spatial heterogeneity, encompassing a wide range of soil burn severity (SBS) levels, varying from low to high (Alexis et al., 2010; Vega et al., 2013). Although changes in OM properties after wildfire have been documented, the mechanisms relating these effects to burn severity are not well understood (Almendros and González-Vila, 2012). In many studies, SBS is not well described. Visual signs of SBS, defined on the basis of the immediate changes in the litter layer and deposition of ash, may be useful for inferring the level of alteration caused by fire in soil. Previous studies (Merino et al., 2014; Neris et al., 2014; Vega et al., 2013) have shown that visual evaluation of SBS can be used to characterize the spatial variability of the post fire degradation of SOM and soil chemical and biological properties.

Analytical techniques such as solid-state ^{13}C NMR and Fourier-transform infrared spectroscopy (FT-IR) are used to characterize the structure and composition of SOM in burnt soils (e.g. González-Pérez et al., 2004). The use of thermal analysis methods, such as differential scanning calorimetry (DSC) and thermogravimetry (TG), which are based on the exothermic decomposition of organic substances, can also be used to characterize certain SOM properties following wildfire and other types of perturbation (Fernández et al., 2011; Leifeld and von Lützow, 2014). These methods are much faster than other techniques, and they can therefore be used in studies requiring analysis of a large number of samples. The combined use of thermal techniques and other analytical procedures enables interpretation of OM thermal properties and provides better characterization of SOM quality (Mastrolonardo et al., 2014; Merino et al., 2014; Neris et al., 2014).

The purpose of this study was to evaluate the amount, composition and quality of the charred biomass generated during burning of the litter layer in five different ecosystems affected by wildfire. The ecosystems were compared by exploring the changes in OM brought about by two different levels of SBS observed in the field immediately after fire. Thermal analysis was used in combination with element analysis, solid-state ^{13}C NMR and Fourier-transform infrared spectroscopy (FT-IR) to characterize the changes in OM quality.

2. Materials and methods

2.1. Study sites

The study was conducted in five sites affected by wildfires in Spain (Fig. 1). Three of the sites are forest stands dominated by *Pinus nigra*, *Pinus pinaster* and *Eucalyptus globulus*. The other two sites are shrubland systems comprising *Erica arborea* and *Ulex europaeus*. The *P. nigra* forest is located in central Spain (Mediterranean climate: average rainfall, 500 mm; average temperature, 13.1 °C). The other sites are located in NW Spain, and the climate conditions are similar in three of them (Atlantic climate: average rainfall, 1700 mm; average temperature, 14.0 °C). Both of the study regions are seriously affected by wildfires (Mataix-Solera and Cerdà, 2009).

The soils are developed from limestone (*P. nigra* site), granitic rock (*P. pinaster*, *E. globulus* and *U. europaeus*), schist and shale (*E. arborea*). Table 1 summarizes the main characteristics of the study sites. In the forest sites, litter layer depth varied from 6.0 to 6.9 cm. The litter layer is thinner (3.5–4.0 cm) in the shrubland sites (measurements carried out during the sampling) than in the forest sites.

2.2. Experimental design and soil sampling

Visual inspection of the different levels of SBS and sampling of burnt and unburnt litter were conducted 3–7 days after fire and before the first rainfall event in the area. Very short and similar intervals between

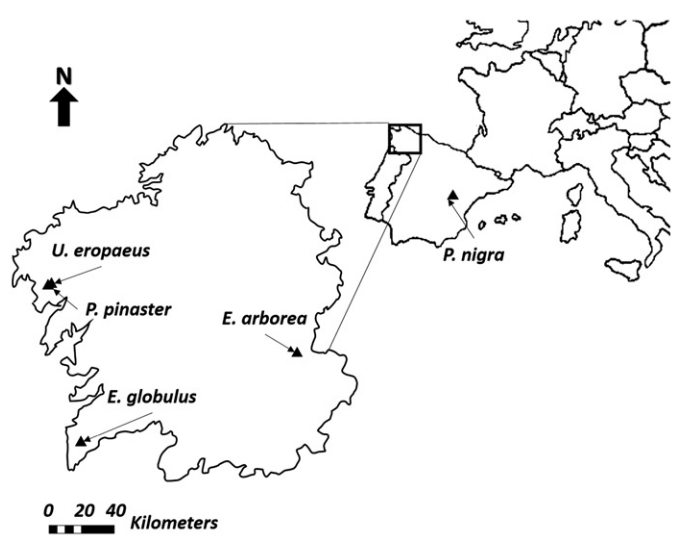

Fig. 1. Location of the five study sites.