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Molecular characterization of wildfire impacts on organic matter in eroded sediments and topsoil in Mediterranean eucalypt stands

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ABSTRACT

Wildfires can increase soil erosion due to the destruction of the vegetation and changes in soil organic matter (SOM) quantity and quality. This fact is especially dramatic in the case of Mediterranean ecosystems. Therefore, the major goal of the present study was to achieve a better understanding of the short-term effects of wildfires on the quantity and quality of organic matter (OM) in the topsoil of burnt Mediterranean eucalyptus plantations in north-central Portugal.

Wildfire had a large impact on slope-scale sediment losses, as they were approximately 30 times higher at the burnt site than at the unburnt site over the first 25 months after the fire. The pH and total nitrogen (TN) content of the burnt topsoil showed a noticeable increase immediately after the wildfire, whereas the total organic carbon (TOC) content revealed the opposite behavior. However, the TOC content showed a partial recovery during the subsequent two years after the fire. The sediments eroded after the fire were consistently more acidic and richer in TOC and TN than the burnt topsoil; they also revealed less pronounced changes with time-since-fire compared with the burnt topsoil.

Analytical pyrolysis analyses indicated that the fire resulted in an enrichment of aromatic compounds, nitrogen (N) constituents, lignin-derived compounds and polysaccharides. The latter is best explained with the input of partially charred OM, ash and decaying parts of plants killed by the fire. The thermal transformation of SOM caused the thermal breakdown and cracking of *n*-alkane compounds, as was revealed by the increase of the ratio of short-to-long chains and the alteration of the typical odd-over-even carbon predominance indexes. The relative abundance of specific biomarkers for vegetation and, in particular for *Eucalyptus globulus*, such as terpenoids eucalyptol and globulol decreased drastically or even disappeared from the pyrolysates of the burnt topsoil. These fire-induced changes in the quality of topsoil OM persisted during the whole post-fire period of 25 months. In general, the Py–GC/MS results pointed out that during the first two years after the fire the recovery of the topsoil OM quality was practically negligible.

1. Introduction

In Portugal, like in other Mediterranean regions in southern Europe, wildfire frequency and extent have increased dramatically during the last decades (Caon et al., 2014; Marques et al., 2011; Shakesby, 2011) and a substantial reduction of the fire frequency is not expected for the next decades (Pereira et al., 2006). This intensification of the fire regime can be attributed to a combination of socio-economic changes, in particular land abandonment and afforestation with fire-prone tree species such as pine and eucalyptus and an increase in meteorological conditions propitious to wildfires (Llovet et al., 2009; Pereira et al., 2006).

As discussed by Shakesby (2011), wildfires can have important effects on soil geomorphologic and hydrological processes. The commonly observed increases in runoff and soil erosion in recently burnt areas are typically attributed to the removal of the protective soil cover by vegetation and litter, in combination with heating-induced changes in topsoil properties such as infiltration capacity, aggregate stability and soil water repellency (Badía-Villas et al., 2014a; Granged et al., 2011; Prats et al., 2014; Shakesby and Doerr, 2006; Varela et al., 2010). The combined direct and indirect effects of fires can have important short- to long-term implications for key aspects of soil quality such as the quantity and quality of soil organic matter (SOM), nutrient stocks and pollutants (e.g., polycyclic aromatic compounds), as well as for aquatic habitats receiving sediment- and ash-loaded runoff from upstream burnt areas (Campos et al., 2012; González-Pérez et al., 2004; Smith et al., 2011).

The observed effects of fire on SOM content are highly variable, depending markedly on fire severity, and may range from (almost) complete destruction to increases of up to 30%, especially in topsoil layers as a result of the incorporation of ash and charred material (De la Rosa et al., 2013). The effects of fire on SOM quality continue an important

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research gap, also because recent advances and, in particular, the use of pyrolysis gas chromatography/mass spectrometry (Py–GC/MS), also called analytical pyrolysis, have shown that these effects can be very complex (Aznar et al., 2013; Badía-Villas et al., 2014a; De la Rosa et al., 2008b, 2012; González-Pérez et al., 2004). Analytical pyrolysis provides information concerning the structure of organic molecules, including N species, which cannot be released by hydrolysis. This technique involves thermolytic fractionation of macromolecules into small fragments that are analyzed by gas chromatography–mass spectrometry (GC–MS). Nonetheless, some fire effects on SOM quality are now well-established such as, the increase of aromatic C at the expense of thermo-labile O-alkyl C due to charring as well as the conversion of peptide N into heterocyclic structures (De la Rosa et al., 2008b; González-Pérez et al., 2008; Knicker et al., 2006). Overall, wildfires can lead to a considerable rearrangement of the C forms in SOM and produce a variety of new substances such as water-repellent compounds and a range of pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans and polychlorinated biphenyls, which may have important repercussions for soil health and quality (Arias et al., 2005; González-Pérez et al., 2008, 2014). Among these pollutants, especially PAHs have been identified as an important risk for downstream aquatic habitats (Campos et al., 2012; Gabos et al., 2001).

The present study aimed to determine the short-term effects of wildfires on SOM quality, in particular by comparing burnt and unburnt topsoil of Mediterranean eucalyptus plantations on four occasions, starting immediately after the first post-fire rain till two years later. In addition, this study also aimed to advance the knowledge of the molecular composition of the OM that is being exported by post-fire overland flow following a wildfire. Investigation of the OM composition of transported sediments is of crucial significance for a sophisticated evaluation of wildfire effects on terrestrial ecosystems as well as the aquifer and downstream waters. To do so, this study heavily relies on Py–GC/MS.

2. Material and methods

2.1. Study areas and site description

This study was carried out in two eucalyptus plantations (*Eucalyptus globulus* Labill.) located near the Ermida hamlet (40° 08′ 46″ N; 7° 59′ 35″ W; 500 m a.s.l.) of the Sever do Vouga municipality, Aveiro District, north-central Portugal (Fig. 1). One of the eucalyptus plantations (EB: eucalyptus burnt) was burnt by a wildfire with moderate severity (Faria et al., 2015; Machado et al., 2015) occurring between the 26th

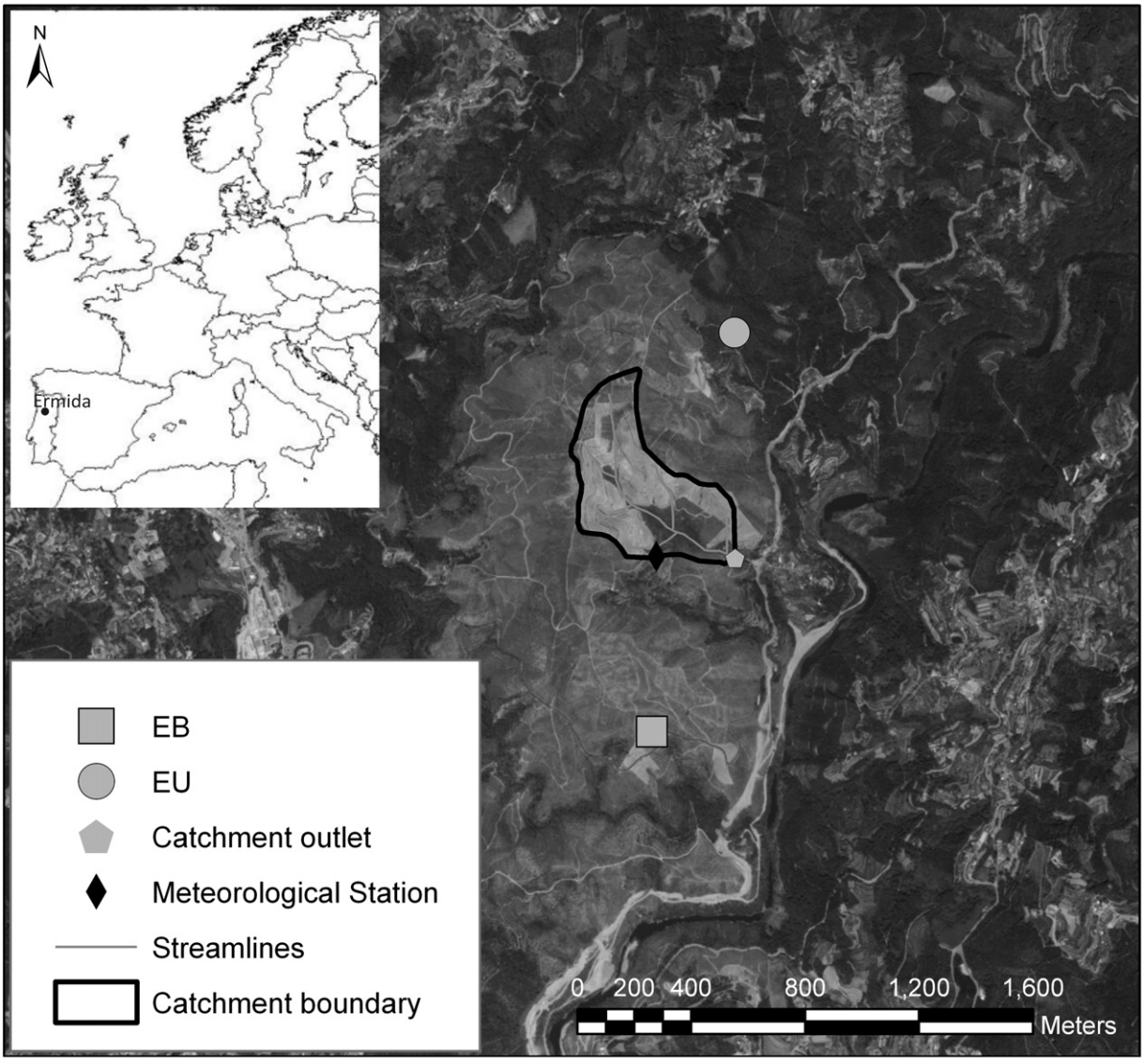

Fig. 1. Location of the Ermida study area and the two study sites, burnt (EB) and unburnt (EU) eucalypt plantations.