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Size fractionation as a tool for separating charcoal of different fuel source and recalcitrance in the wildfire ash layer

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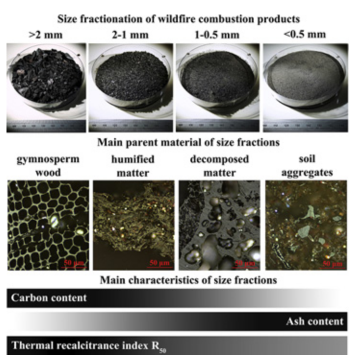
HIGHLIGHTS

- Combustion products from two forest wildfires with different severity were analysed.
- Collected material was divided into four size fractions (>2, 2–1, 1–0.5, <0.5 mm).
- Size fractionation allowed isolating charred material with distinct properties.
- Specific source fuels were preferentially sorted into specific size fractions.
- Mineral ash content is a reliable indicator for selecting the best fractions to isolate.

GRAPHICAL ABSTRACT



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ABSTRACT

Charcoal is a heterogeneous material exhibiting a diverse range of properties. This variability represents a serious challenge in studies that use the properties of natural charcoal for reconstructing wildfires history in terrestrial ecosystems. In this study, we tested the hypothesis that particle size is a sufficiently robust indicator for separating forest wildfire combustion products into fractions with distinct properties. For this purpose, we examined two different forest environments affected by contrasting wildfires in terms of severity: an eucalypt forest in Australia, which experienced an extremely severe wildfire, and a Mediterranean pine forest in Italy, which burned to moderate severity. We fractionated the ash/charcoal layers collected on the ground into four size fractions (>2, 2–1, 1–0.5, <0.5 mm) and analysed them for mineral ash content, elemental composition, chemical structure (by IR spectroscopy), fuel source and charcoal reflectance (by reflected-light microscopy), and chemical/thermal recalcitrance (by chemical and thermal oxidation).

At both sites, the finest fraction (<0.5 mm) had, by far, the greatest mass. The C concentration and C/N ratio decreased with decreasing size fraction, while pH and the mineral ash content followed the opposite trend. The coarser fractions showed higher contribution of amorphous carbon and stronger recalcitrance. We also observed that certain fuel types were preferentially represented by particular size fractions. We conclude that the differences between ash/charcoal size fractions were most likely primarily imposed by fuel source and secondarily

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by burning conditions. Size fractionation can therefore serve as a valuable tool to characterise the forest wildfire combustion products, as each fraction displays a narrower range of properties than the whole sample. We propose the mineral ash content of the fractions as criterion for selecting the appropriate number of fractions to analyse.

1. Introduction

Every year wildfires affect over 3% of Earth's vegetated land surface (Randerson et al., 2012), which has large direct consequences for the global carbon (C) cycle because of the transformation of a large amounts of organic matter (OM) to CO_2 (Alexis et al., 2007). However, wildfires do not imply complete combustion of OM (González-Pérez et al., 2004; Certini et al., 2011), and the incomplete combustion residue produced is a carbon-rich heterogeneous black material, typically characterised by a condensed aromatic structure. This material can accumulate on the ground in large quantities across the burned area, and is referred to as pyrogenic organic matter (PyOM) or pyrogenic carbon (PyC) (Santín et al., 2016a). PyOM represents a continuum of materials showing a different degree of carbonization, which ranges from slightly charred biomass to highly condensed soot (Masiello, 2004).

Within this continuum, charcoal comprises coarse particles (mm-cm) that retain the physical and chemical properties allowing to identify its biomass source (Bird and Ascough, 2012; Knicker et al., 2008; Scott, 2010). The aromatic structure gives charcoal an inherent increased resistance to biotic and abiotic degradation (Eckmeier et al., 2007; Wiechmann et al., 2015), which is further increased once the charcoal is buried in soil, due to enhanced physical protection, to an extent that charcoal is a common source of paleoenvironmetal and archaeological proxy data (Ascough et al., 2008).

However, charcoal is a heterogeneous material (Bird and Ascough, 2012; Pyle et al., 2015), whose variability is mostly due to differences in burning conditions (in terms of temperature, duration, flaming or smouldering conditions, oxygen availability *et cetera*) and source materials (*e.g.* woody or grass vegetation, leaves or branches, conifers or broadleaves) (Bodí et al., 2014; Knicker et al., 2008; Merino et al., 2015; Santín et al., 2012; Wiechmann et al., 2015) and their interactive effect (Hatton et al., 2016). Therefore, charcoal heterogeneity is particularly high in fire affected natural forest ecosystems, due to an often wide diversity of species, fuel types, structure and density, combined with a high spatial and temporal variability in fire behaviour (temperature, flame residence time, oxygen availability) in a given fire (Pyle et al., 2015; Santín et al., 2016b).

The variability of charcoal composition and structure has obvious implications for charcoal fate in the environment (McBeath et al., 2013; Santín et al., 2016b) and, hence, on its role in the global carbon cycle (Bird et al., 2015; Santín et al., 2016a). Therefore, an important research need is to disentangle the complex nature of charcoal. In context, some authors have previously reported size fractionation as a means to separate charcoal pools with contrasting composition (*i.e.* Nocentini et al., 2010; Rumpel et al., 2007; Francioso et al., 2011). In spite of its simplicity, however, this technique is not yet extensively used to characterise wildfire combustion products. As highlighted by Michelotti and Miesel (2015), the current knowledge on charcoal composition and fate is primarily based on studies dealing with charcoal produced under experimental conditions in the laboratory, which it is not fully representative of charcoal from wildfires (Alexis et al., 2010; Belcher and Hudspith, 2016). More research on natural charcoal is therefore needed.

This study focuses on the ash/charcoal layer from two forests burned at different severities. This material was fractionated into four different size fractions (>2, 2–1, 1–0.5, <0.5 mm) with the aim to ascertain to which extent particle size fractionation is a reliable method to obtain specimens with distinct composition. The size and number of fractions were those chosen by Nocentini et al. (2010), in order to have a direct basis of comparison with the results of their work. Of these fractions we also evaluated the thermal recalcitrance using the thermal recalcitrance index (R_{50}) developed by Harvey et al. (2012) for biochar, *i.e.* charcoal produced under controlled standard conditions. Here, for the first time, we tested to see if this index could also be applicable to wildfire charcoal.

2. Materials and methods

2.1. Study sites

The study sites were Orentano (hereafter called OR), 30 km east of Pisa, Central Italy, and Mount Gordon (hereafter called MG), near Marysville, in the State of Victoria, south-east Australia.

OR (coordinates WGS84: 43°47′22.82″N, 10°39′52.30″E) has an elevation of 20 m a.s.l., a mean annual precipitation of 893 mm and a mean annual temperature of 14.3 °C. The vegetation cover was a mixed forest of Downy oak (*Quercus pubescentis* Willd) and Maritime pine (*Pinus pinaster* Aiton) with a thick understory of common fern (*Pteridium aquilinum* L.) and *Rubus* spp. In July 2011, an area of 3.3 ha underwent a wildfire considered ‘moderately to highly severe’ using the visual scales of litter and vegetation consumption proposed by Chafer et al. (2004). Most of the tree stems were still standing after the fire, partly or totally scorched, while the soil was covered by an ash/charcoal layer with very little or no uncharred litter remaining. This layer was sampled three days after the fire, prior to any rain. Additional information about the site, including a picture of the burned area, is reported in Mastrolonardo et al. (2015a).

The climate at MG, is characterised by a mean annual precipitation of 670 mm and mean annual temperature of 13 °C. The site was chosen because it represented an end-member in terms of fire severity. It was affected by the so-called ‘Black Saturday fire’ in early February 2009. Fireline intensity was estimated to have exceeded 70,000–80,000 kW m^{-1}, which is one of the highest reported in Australia (2009 Victorian Bushfires Royal Commission, 2010). The sampling site (37°31′56.30″S, 145°43′17.14″E) is 3 km SW of Marysville, on the road to Narbethong, 530 m a.s.l. in elevation. It was a *Eucalyptus* spp. forest and the wildfire removed the entire litter layer, green vegetation, and woody stems < 10 mm in diameter. Accordingly, fire severity was classified as ‘extreme’, based on the classification of Chafer et al. (2004). Sampling was performed in April 2009, two months after the fire and following some light rainfall, but before the more intense precipitations of winter had caused any significant mixing or removal of material from the ash/charcoal layer could occur *via* erosion. Additional information about the site, including pictures of the burned area, is reported in Mastrolonardo et al. (2015a) and Santín et al. (2012).

In addition, we used published data from another study site, Migliarino (hereafter, MI), described by Nocentini et al. (2010), for a direct comparison to our study site OR given their proximity and similarity in terms of vegetation. MI, which is located 30 km west of Pisa, had a *Pinus pinea* L. forest with a tangled bushy understory of *Quercus ilex* L., *Smilax aspera* L. and *Erica arborea* L. that was affected in July 2007 by a wildfire of ‘high to very high’ severity (Certini et al., 2011), based on the classification of Chafer et al. (2004).