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Abundance and composition of free and aggregate-occluded carbohydrates and lignin in two forest soils as affected by wildfires of different severity

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ABSTRACT

Organic matter is the soil component most affected by wildfires, both in terms of abundance and composition. Fire-induced alteration of soil organic matter (SOM) depends on heating intensity and duration, oxygen availability and other factors related to topography, climate, soil and vegetation features. Particularly affected by fire is the litter layer, but SOM from the uppermost mineral soil can also experience some major changes. In this study, we investigated the direct impact of fire on molecular SOM parameters in density fractions isolated from the top 2.5 cm of mineral soil in two forests that recently experienced wildfires of different severity. One, located in Tuscany, Central Italy, is a mixed forest of Downy oak and Maritime pine, developed on Acrisols formed on sandy lacustrine deposits, affected by a moderately severe fire. The other, located in Victoria, South-East Australia, is a mixed-species eucalypt forest, developed on a Cambisol formed on sandy Devonian sediments, affected by an extremely severe fire (the infamous 'Black Saturday' fire). The purpose of this study was the assessment of fire-induced changes on amount and composition of the bulk SOM and SOM associated to soil fractions having different densities. We used 1.8 Mg m^{-3} as density cut-off and distinguished between free and aggregate-occluded SOM. In particular, the analyses focused on abundance and composition of two major SOM components, proposed as molecular indicators of fire severity: the non-cellulosic neutral sugars, digested by trifluoroacetic acid (TFA), and the lignin-derived phenolic monomers, released by cupric oxide (CuO) oxidation. The chemical structure of both bulk SOM and SOM fractions were analysed by solid-state ^{13}C nuclear magnetic resonance spectroscopy.

In contrast to the moderately severe fire affecting the Italian site, the extremely severe fire at the Australian site caused substantial loss of SOM from the top mineral soil. Both fires had major effects on SOM composition. In spite of the evident impact they experienced, neither hydrolysable sugars nor lignin phenols resulted to be reliable indicators of fire severity. Moreover, both fires apparently broke up soil aggregates, hence promoting the release of some occluded organic matter. The fire-induced changes of SOM observed have implications for the C cycle, so highlighting the critical role of wildfire occurrence and severity in climate change.

1. Introduction

Fire is a major ecological factor, affecting more land surface than any other natural disturbance (Lavorel et al., 2007; Scott et al., 2014). Soils suffer many direct and indirect consequences of fire, which can involve the physical, mineralogical, chemical and biological properties, either temporarily or permanently (Bento-Gonçalves et al., 2012; Certini, 2005; Neary et al., 1999). The organic component of soil is the one most impacted by fire, in terms of both content and composition (González-Pérez et al., 2004; Certini et al., 2011). The assessment of the overall effect of fire on soil organic matter (SOM) is a complex task because burnt soils are generally a patchwork of areas affected by burning to different degrees. Actually, besides the factors correlated with site, soil and vegetation features, differences in heating intensity and duration, oxygen availability and type of combustion (smouldering or flaming), may induce different SOM transformations (González-Pérez et al., 2004; Rumpel et al., 2007; Shakesby and Doerr, 2006). Most often fire causes a substantial reduction or even complete removal of the litter layer (Bento-Gonçalves et al., 2012; Certini et al., 2011; Nave et al., 2011). However, inconsistent results regarding quantitative changes in the mineral soil are reported in the literature. For instance, meta-analyses by

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Johnson and Curtis (2001) and Nave et al. (2011) have contrasting outcomes, concluding that, in the short-term, the A horizon does experience, respectively, a significant fire-induced increase or decrease in C content. However, divergent results from different studies can arise from methodological discrepancies, related to sampling strategy, including soil depth interval considered, the time elapsed since fire, as well as local conditions, as for example vegetation/climate type.

In terms of SOM quality, the reactions that occur during combustion, i.e., dehydration, dehydrogenation, volatilisation of nitrogenous compounds, decarboxylation, demethylation, demethoxylation, cyclisation and polycondensation (Hernández et al., 1997; Knicker, 2007), can substantially change the composition of the parent material. Charcoal formation is the most common outcome of wildfires and essentially represents the temperature and oxygen-depletion dependent transformation of the organic compounds into highly recalcitrant aromatic structures (Alexis et al., 2010). Once incorporated into the soil, charcoal may resist decomposition for centuries or even millennia, thereby sequestering carbon (Egli et al., 2012; Kuhlbusch and Crutzen, 1995; Schmidt and Noack, 2000). Carbohydrates are believed to be among the components of SOM most easily affected by fire (Certini, 2005; González-Pérez et al., 2004; Knicker et al., 2006). On this basis, Martín et al. (2009) proposed the ratio of carbohydrates to total SOM as an index of fire impact on SOM quality. In principle, such an index also allows low and high soil burn severity wildfires to be differentiated. Lignin, which, after carbohydrates, is the second most abundant component of plant residues in terrestrial ecosystems, is rather resistant to fire and is totally oxidised only at 400–450 °C (DeBano, 1991; Kuo et al., 2008). Nevertheless, despite the high heat resistance of its backbone (Knicker, 2011; Sharma et al., 2004), lignin is affected by fire at much lower temperatures (200–250 °C), at least in terms of the distribution of phenols (Certini et al., 2011; Nocentini et al., 2010; Rumpel et al., 2007). Therefore, the phenolic composition of lignin has potential as an indicator of fire occurrence and severity. Quantifying post-fire lignin phenols and sugars in soil might be useful to evaluate the wider impact of fire on soil quality.

In the mineral soil, the effects of fire are usually confined to the top few centimeters because of the low thermal conductivity of both minerals and air in pore spaces. Therefore, it is important to avoid sampling at substantial depths, because this is likely to result in a dilution of the fire effects on soil.

In this study, we investigated the top 2.5 cm of mineral soil of two forests, located in Italy and Australia, which had been affected by recent wildfires of moderate and extreme severity, respectively. The purpose of using two contrasting sites in terms of forest type and fire severity was to assess changes to SOM quality resulting directly from the fire and explore its implications. We focused particularly on the non-cellulosic neutral sugars, i.e., those digested by trifluoroacetic acid (TFA), and lignin-derived phenolic monomers, i.e., those released by cupric oxide (CuO) oxidation. The changes SOM experienced at the two sites were compared and contrasted, hypothesising common fire-related alterations in SOM mainly driven by fire severity. Furthermore, we analysed the quantity and composition of SOM allocated to soil fractions having different densities, distinguishing between free and aggregate-occluded SOM.

2. Materials and methods

2.1. Study sites

The study sites were Orentano, 30 km east of Pisa, Tuscany, Central Italy, and Mount Gordon, near Marysville, in Victoria State, South-East Australia (Fig. 1; Table 1).

Orentano (hereafter called OR), 20 m a.s.l., has a mean annual precipitation of 893 mm and a mean annual temperature of 14.3 °C. The vegetation cover is a mixed forest of Downy oak (*Quercus pubescentis* Willd) and Maritime pine (*Pinus pinaster* Aiton) with a rich understory of common fern (*Pteridium aquilinum* L.) and *Rubus* spp. Soils formed on sand and stony lacustrine deposits – where quartz is largely dominant and chlorite, illite, kaolinite, and goethite are accessory minerals – and are classified as Haplic Skeletic Acrisols according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). In July 2011, an area of 3.3 ha underwent a wildfire of moderate severity, based on the visual scale of litter and vegetation consumption proposed by Chafer et al. (2004). Most of the tree stems were still standing after the fire and were partly or totally scorched. The soil was entirely covered by charcoal and ash, with no or very little uncharred litter remaining. Soil sampling was carried out three days after the fire on both the burnt area (coordinates WGS84: 43°47′22.82″N, 10°39′52.30″E) and an adjacent (50 m away) unburnt area having the same characteristics of the burnt one prior to fire occurrence, hence used as control.

At Mount Gordon (hereafter called MG) the sampling area is located 530 m a.s.l., where mean annual precipitation is 670 mm and mean annual temperature is 13 °C. The site was chosen because it represented an end-member in terms of fire severity. The sadly famous 'Black Saturday' fire, which involved also MG, in early February 2009, burned about 450,000 ha of eucalypt forest causing the loss of 173 lives (Royal Commission, 2009). Average fire-line intensity is estimated to have exceeded 70,000–80,000 kW m^{-1}, which is among the highest ever reported in Australia (Royal Commission, 2009). The extreme fire intensity was promoted by particularly extreme weather conditions, such as wind speeds up to 100 km h^{-1} and air temperatures even exceeding 45 °C. Fuel loads were very high, since the forest had not experienced a major fire since 1939 (fuel load, including the litter, amounted to 25–40 Mg ha^{-1}), and fuel moisture was very low (3–4%) because of prolonged drought conditions (McCaw et al., 2009). The sampling site (37°31′56.30″S, 145°43′17.14″E) is a *Eucalyptus* spp. mixed forest 3 km SW of Marysville on the road to Narbethong. The fire removed all ground fuel, 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). A long unburnt site, approximately 3 km NW of Narbethong (37°32′54.10″S, 145°37′37.30″E) – last burnt by wildfire in 1939 – was selected as control. This site is 8.5 km away from the burnt site and as much as possible similar to the latter in terms of all environmental conditions, soil included. Soils of the area formed on sandy Devonian sediments – where quartz largely prevails and the clay-size fraction comprises vermiculite, illite, and kaolinite – and are classified as Dystric Humic Cambisols according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). Sampling was performed in April 2009, two months after the fire and following some light rainfall, but before the more intense winter precipitations had caused significant ash removal via erosion.

2.2. Soil sampling

At both OR and MG study sites the sampling involved four parallel 20 m transects, 5 m apart, at 5 m intervals. Twenty mineral soil samples were taken at each site down to 2.5 cm, after carefully removing the ash, charcoal, or any litter layer by a brush. In both burnt areas, ten samples of charcoal particles were randomly collected in 40 × 40 cm plots.

2.3. Physico-chemical properties

Soil pH was measured potentiometrically using deionised water to soil ratio of 5:1, while particle size analysis was performed according to the hydrometer method. Total C and N contents and stable carbon isotopic composition of the fine earth (the less than 2 mm soil fraction) and charcoal were measured by a Carlo Erba NA1500 elemental analyser coupled to an isotope ratio mass spectrometer (Micromass-Optima). δ^{13}C isotope abundance was reported in per mil (‰) relative to the Pee Dee Belemnite standard (PDB).