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Application of thermal and spectroscopic techniques to assess fire-induced changes to soil organic matter in a Mediterranean forest

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ABSTRACT

Organic matter is the soil component most sensitive to fire, being the fuel on the ground and below. It is affected by fire in terms of both abundance and composition. Incomplete combustion yields condensed carbon forms characterized by higher recalcitrance to biological and chemical attack compared to the parent material. In this study, thermogravimetry (TG-DTG), differential scanning calorimetry (DSC), attenuated total reflectance/Fourier transform infrared spectroscopy (ATR/FT-IR), and Raman spectroscopy were applied to (1) charcoal particles accumulated on the ground, (2) the top 10 cm of soil, and (3) the organic matter extracted using an alkaline solution, to investigate the wildfire effect on the organic pool of the loamy and sub-acid soil of a maritime pine (*Pinus pinaster* Ait.) forest. The same investigations were performed on the litter layer and the mineral soil of an adjacent unburnt area, similar to the burnt one before fire occurrence. TG-DTG and DSC measurements highlighted an accumulation of soil organic matter (SOM) in the burnt soil, which suggests an incorporation of partly charred necromass into soil and the formation of pyrogenic highly refractory organic matter, i.e. black carbon. The ATR/FT-IR showed changes in the fire affected extractable SOM compatible with the formation of stable N containing compounds, which was well confirmed also by the presence of CN group vibration in the Raman spectrum. The combined application of thermal and spectroscopic techniques resulted to be highly useful to rapidly estimate many of the effects of fire on soil organic matter.

1. Introduction

In order to completely understand the role of soils as carbon stores, it is essential to evaluate the vulnerability of soil organic matter (SOM) to anthropic or natural disturbances, as well as to characterize and identify SOM fractions with short versus long residence times (Smith, 2005). Fire is a major disturbance and driving factor of ecosystems, especially in those with Mediterranean type of climate, where higher fire frequency is expected in the next future due to climate change (Moriondo et al., 2006) and anthropic activities (Pausas et al., 2008). In the Mediterranean areas, soils are dramatically impacted by wildfires, especially because of post-fire erosion, which upset or even remove the topsoil (Shakesby, 2011). Many and important, however, are also the direct effects of fire (Certini, 2005). In particular, the organic component of soil, which is the fuel in soil, is affected in terms of both abundance and composition (González-Pérez et al., 2004; Knicker, 2007). The superficial organic horizon is partly or totally removed by wildfires (Certini et al., 2011), while in terms of composition, SOM become more heterogeneous due to fire. Apparently, in fact, no original component disappears and, on the other hand, new thermally-condensed aromatic compounds form as a consequence of chemical reactions induced by high temperatures (Francioso et al., 2011; González-Pérez et al., 2004; Knicker, 2007). These fire-derived compounds are collectively called pyrogenic organic matter (PyOM) and are reported to have generally longer residence time in soil compared to the original materials (Schmidt and Noack, 2000).

No single analytical method can adequately account for the continuum of materials that form during fire; therefore a multiple-technique analytical approach is required to describe the chemical complexity of PyOM. Thermal analyses, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG), have been used since a long time for the determination of basic properties of soil (Siewert, 2004), in particular to characterize its organic component (e.g. Alexis et al., 2010; Barros et al., 2011; Fernandez et al., 2011; Francioso et al., 2005; Tonon et al., 2010). Although the

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results obtained by such techniques on the effect of heating on SOM under laboratory conditions are promising and several papers were published in this regard, there is much less information dealing with in situ studies. The use of thermal techniques offers the unique opportunity to directly measure changes in thermal stability of SOM as a function of heating effect (Plante et al., 2009) and might be fruitfully used to distinguish PyOM from other SOM fractions, which is still an unfulfilled task (Leifeld, 2007; Reeves et al., 2008). However, in terms of chemical structure thermal methods do not provide information equivalent to the one from other types of analysis, e.g. spectroscopic techniques (Plante et al., 2009). Also infrared spectroscopy has been successfully applied to characterize PyOM and charcoal, especially whether in combination with Raman spectroscopy (Francioso et al., 2011; Lammers et al., 2009; Nocentini et al., 2010). In fact, aromatic bonds with different substitutions respond directly to infrared spectroscopy, while Raman spectroscopy provides valuable information on both aliphatic and aromatic skeletal structure. However, spectroscopic analyses have the limit to be modestly influenced by the physical arrangement of molecules and macro-structures, which strongly affects the thermal stability of materials (Plante et al., 2009). Therefore, combining spectroscopic and thermal techniques appears to be convenient to study PyOM.

In the present study, we used thermal (TG and DSC) and spectroscopic (FT-IR and Raman) analyses to assess the direct effects of a wildfire on SOM structure and composition in a Mediterranean pine forest. For this purpose, we compared and contrasted a burnt area and an adjacent unburnt area virtually homogeneous prior to fire occurrence. We focused on the organic matter on the ground – handpicked charcoal particles in the case of the burnt site and litter in the case of the unburnt site – the bulk underlying mineral soil, and the SOM extracted from the latter.

2. Materials and methods

2.1. Study site

The study was carried out in a maritime pine forest located at 42° 54′ 14.17 ″N, 11° 08′ 48.99 ″E, in the municipality of Roccastrada, Southern Tuscany, central Italy, 25 km away from the coast and 360 m above sea level (Fig. 1). The site experiences a mean annual temperature of 13.5 °C and a mean annual precipitation of 897 mm, mainly concentrated in autumn and early spring. The forest is dominated by maritime pine (*Pinus pinaster* Ait.) with scattered ancillary trees of *Quercus suber* L. and *Quercus ilex L.* The understorey is heterogeneous and composed of shrub species typical of the Mediterranean maquis, such as *Arbutus unedo* L. and *Erica* spp. The soil, which developed on a metamorphic formation mainly comprising quartzite and schist sandstone, shows an O-A-Bw-C sequence of horizons and is classified as Dystric Episkeletic Cambisol according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006).

The wildfire considered in this study occurred in July 2010 and involved an area of 33 ha, where the forest had been just cut because of sanitary reasons and the felled logs were sparsely lying on the ground. Based on the amount of canopy burnt and ground observations using visual scale of fire severity proposed by Chafer et al. (2004), the severity of the wildfire in question was classified as “very high”, which means almost complete consumption of litter, shrubs, tree canopies and less than 5 mm stems.

2.2. Sampling

Sampling was performed 2 months after the fire occurrence. At that time, a charcoal and ash layer covered the burnt area, only disrupted by scattered sprouts. The sampling was carried out in six plots from the burnt area and six from an adjacent area where fire did not run because of being stopped by a permanent track. At each plot the organic matter lying on the mineral soil (ash/charcoal layer in the burnt area and litter layer in the unburnt area) was sampled within a 40 for 10 cm frame, using a trowel and a brush. Thereafter, the mineral soil was sampled by a spade down to 10 cm, cutting a 15 for 15 cm wide slice. All samples were left to air dry in the laboratory to constant weight. The organic material, charcoal or litter, was finely ground (saving an intact aliquot), while the mineral soil was screened through a 2 mm mesh sieve and just the fine earth (<2 mm fraction) ground in a ball mill before analyses. Equal aliquots of the independent samples were combined to make a single sample from either area to undergo investigation.

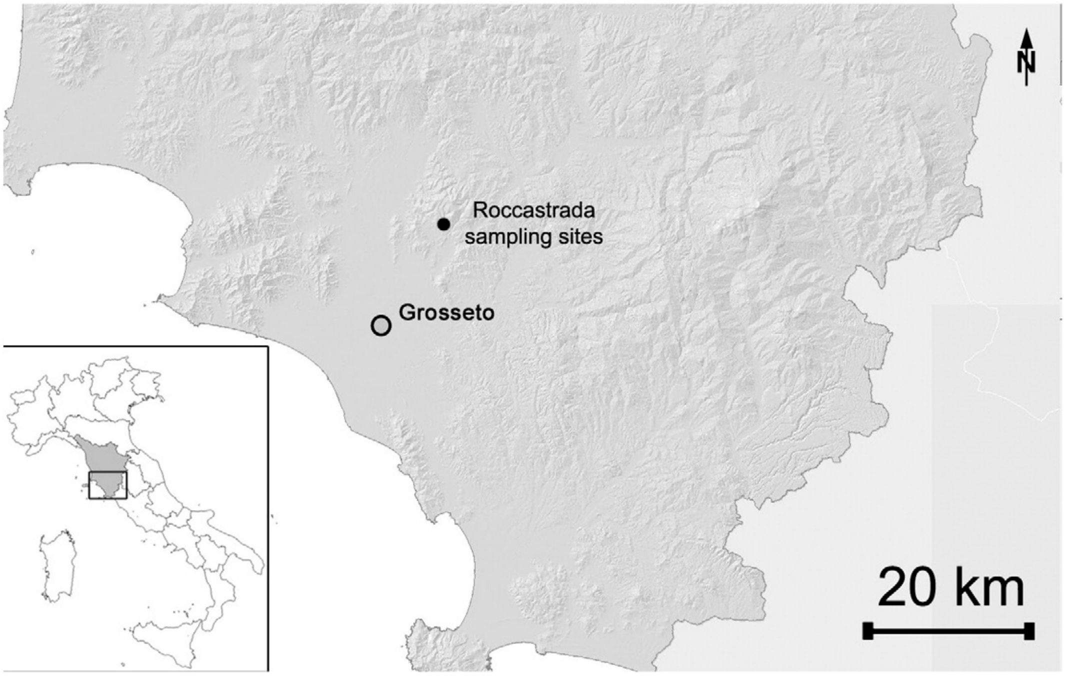

Fig. 1. Location of the study area, Roccastrada, southern Tuscany, central Italy.