



# Severe wildfire hinders renewal of soil P pools by thermal mineralization of organic P in forest soil: Analysis by sequential extraction and $^{31}\text{P}$ NMR spectroscopy

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## ABSTRACT

Forest productivity is limited by soil P availability in several forest ecosystems worldwide. Most of the soil available P is probably produced by the mineralization of organic forms of P when these forms dominate in the soil. Severe wildfires lead to loss of soil organic compounds and therefore represent a strong risk of loss of soil P. The objective of the present study was to examine how the temperature reaching during burning affects the P fractions in organic horizons and soil. For this purpose, we conducted experimental burns of intact soil monoliths with their organic horizons. We then used Hedley chemical sequential fractionation and  $^{31}\text{P}$  MNR spectroscopy to determine the effects of temperature during burning on soil P fractions. In the unburned organic horizons, the organic P represented 70% of the total P and it was completely mineralized when the temperatures reached above 500 °C. Similarly, in the unburned mineral soil, organic P forms represented 76% of the total P and the organic P was reduced by around 50% in the moderate soil burn severity (SBS) levels. In the highest SBS, the concentration of inorganic P (Pi) with a fast turnover rate (representing available P) was three times higher and the concentration of Pi with a slow turnover rate (representing the sum of inorganic fractions bound to Al and Ca) was eight times higher than in the unburned soil. By contrast, the organic P fractions decreased with the temperature reached during the fire, with 200 °C considered a threshold for the total thermal mineralization of organic P, mainly the labile organic fraction. These findings suggest that high temperatures lead to release of Pi, most of which is precipitated by P forms such as Pi with a slow turnover rate. It appears that the high burn severity associated with temperatures higher than 200 °C strongly disrupts soil P dynamics, increasing the occlusion capacity and decreasing the bioavailability.

## 1. Introduction

Many forest ecosystems throughout the world are strongly threatened by wildfires (Scott et al., 2014). The frequency of large wildfires has increased in recent times due to climate anomalies in several forest ecosystems (Liu and Wimberly, 2015, 2016; Gil-Tena et al., 2016). As a consequence of erosion and also chemical and thermal changes, wildfires strongly affect the nutrient dynamics of forest floor via burning of litter, volatilization of soil organic matter and changes in the composition of the soil microbial community (Certini, 2005). Temperatures as high as 700 or 800 °C can be reached during wildfires (Vose et al.,

1999). This leads to loss of most organic C and N as these are volatilized at temperatures above 200 °C (Raison, 1979; Certini, 2005). Several authors have reported C and N losses from litter of around 75%, as well as important changes in soil organic matter (SOM) composition in different forest ecosystems after severe wildfire (Baird et al., 1999; Murphy et al., 2006; Neary and Overby, 2006). The mineral soil is also affected by wildfire, although to a lesser extent than the litter (Certini, 2005). Various authors have reported that at highest soil burn severity (SBS) in the first 10 cm of soil, the concentrations of C and N decrease by around 50% as a direct result of combustion (Kutiel and Naveh, 1987; Baird et al., 1999; Gonzalez-Perez et al., 2004; Murphy et al.,

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2006; Martín et al., 2012; Vega et al., 2013). The losses may continue after the fire event as a result of mineralization and soil erosion (Neary et al., 2005). Burning favors the loss of labile C and increases of around 50% in aromatic (aryl) compounds (Gonzalez-Perez et al., 2004; Preston and Schmidt, 2006; Merino et al., 2014), thus reducing the availability of organic C to the microbial community (Vega et al., 2013).

Forest stands established in acidic soils are constrained by P availability, because this nutrient is strongly precipitated by iron and aluminum ions. Furthermore, in well developed soils, most of the P occurs as organic P (Walker and Syers, 1976; Gil-Sotres et al., 1990; Crews et al., 1995; Cade-Menun et al., 2000; Turner et al., 2007). In such soils, most of the available P is produced by mineralization of organic P, and therefore, the microbial community plays a key role by producing extracellular enzymes that cleave to soil organic compounds and thus release available inorganic P (Walker and Syers, 1976; Turner et al., 2007; Waring et al., 2014).

The Hedley P-extraction method overestimates the amount of organic P in acid soils (Turner et al., 2005). Fortunately,  $^{31}\text{P}$  NMR spectroscopy has proved an accurate tool for the identification and quantification of soil organic P fractions (Cade-Menun, 2005). Thus, the combined use of chemical extractions and  $^{31}\text{P}$  NMR spectroscopy facilitates study of soil P dynamics and enables a better understanding of the changes in P soil dynamics that occur in wildfire with different levels of soil burn severity (SBS). Diester forms of P (P-dieters) are the preferred substrate in P-limited ecosystems (Karl, 2014; Tapia-Torres et al., 2016), although monoester forms (P-monoesters) may also be an important source of available P in most soils (Turner et al., 2003a). P-dieters and two hydrolysable P-monoesters (phosphatidic acid and  $\beta$ -glycerophosphate) are considered labile due to their weak adsorption, while the P-monoesters *scyllo*-inositol and *myo*-inositol are much more stable, because they have higher charge densities and thus react strongly with both organic and inorganic soil compounds (Turner et al., 2003b). These organic labile forms are thus critical for ensuring the long-term availability of soil P for plant production. Any reduction in this P pool may greatly reduce the source of available P in acidic forest soils.

The concentration of inorganic P in soil increases after fire due to input of ash (Kutiel and Naveh, 1987; Giardina et al., 2000; Martín et al., 2012) and to the thermal mineralization of organic P (Kutiel and Naveh, 1987; Cade-Menun et al., 2000; Certini, 2005; Turrion et al., 2010). This leads to more inorganic P being available to plants and soil microorganisms (Kutiel and Naveh, 1987; Murphy et al., 2006) and also makes the P more susceptible to loss by leaching. Moreover, the increased availability is temporary because the P is precipitated by cations, which are also released by thermal mineralization of organic matter (Kutiel and Naveh, 1987; Cade-Menun et al., 2000; Murphy et al., 2006; Durán et al., 2008; Chen and Shrestha, 2012).

Although organic P dominates in many forest soils worldwide, few studies have analyzed the changes in organic P brought about by wildfire. Thermal mineralizations of organic P and consequent increases in the inorganic P have been observed in burned soils (Cade-Menun et al., 2000; Turrion et al., 2010). According with these studies, the labile organic P (orthophosphate diesters), which represents the main source of soil available P, is more vulnerable to mineralization induced by high temperatures, and it decreases in a greater proportion after fire than orthophosphate monoesters (Turrion et al., 2010). However, no studies have yet analyzed the effect of temperature and/or soil burn severity on P biogeochemistry.

Forests growing under the Mediterranean climate regime are highly vulnerable to wildfire. This is particularly true in the temperate-humid zone because of the large amount of biomass that accumulates during the wet season and that becomes highly flammable during the dry summers (Shakesby, 2011; Vega et al., 2013). These conditions are characteristic of forests in NW Spain, and severe wildfires are common in the region (Vega et al., 2013). The forest soils in this region are

characterized by high amounts of organic matter, and as most of the total soil P occurs as organic P (> 70%; Gil-Sotres et al., 1990), these soils are highly susceptible to being affected by severe wildfire. Temperatures higher than 600 °C can be reached in wildfires and a spatial mosaic with different levels of soil burn severity is created depending on the temperature reached at different points (Vega et al., 2013). The effects of fire on soil properties therefore vary depending on the temperature reached during burning. In sites affected by severe burning, increased soil pH, release of cations and inorganic P from organic matter and a strong reduction in organic matter, which becomes dominated by recalcitrant compounds, are observed (Vega et al., 2013; Merino et al., 2014). However, the temporary availability of soil P decreases after the first growth season (Durán et al., 2008). Forest plantations may be strongly limited by soil P because P extraction via wood harvesting is similar to or higher than the available P soil reserves (Merino et al., 2005). Lower phosphatase activity has been recorded (Vega et al., 2013) at moderate SBS, with temperature lower than 200 °C.

The aim of the present study was to examine how different levels of the temperatures reached during burning affect the P fractions in litter and soil from pine forest at NW Spain. Use of this approach enabled us to relate the temperatures reached during fire and also the level of soil burn severity (as a proxy for fire conditions) to the changes in P fractions. We hypothesized that the most labile organic P may be affected by relative low temperatures. Severe wildfires would thus affect the long-term availability of P in soil. To test this hypothesis, we carried out a controlled burning experiment in a wind tunnel, in which we burned intact soil monoliths with vertical heat transmission, simulating wildfire conditions, to yield different levels of soil burn severity. In order to obtain further information about P biogeochemistry, we used a methodological approach combining chemical sequential fractionation and  $^{31}\text{P}$  MNR spectroscopy to extract and analyze the P fractions.

## 2. Materials and methods

### 2.1. Study site

Soil monoliths were collected from a homogenous area of *Pinus pinaster* (maritime pine) forests located from the Galicia (Ria Villagarcía, NW Spain) coastal. Climate is oceanic temperate with mean annual rainfall between 1850 mm and 2565 mm, whereas annual temperature is 14 °C. Soils are aluminic-humic umbrisols (IUSS Working Group WRB, 2014) developed on granitic bedrock. Stand density is averaged 800 trees/ha, diameter at breast height (d.b.h.) is ranged between 22 and 35 cm and tree height ranged between 14 and 24 m. Fern (*Pteridium aquilinum*) has the larger cover in the understory and *Erica cinerea*, *Erica umbellata* and *Frangula alnus* are also frequent.

### 2.2. Experimental design

Undisturbed soil monoliths ( $n = 48$ ) were collected in pairs, at randomly selected points, including their corresponding organic horizons, litter (Oi), fermentation (Oe) and humus (Oa) layers (Brady and Weil, 2002). Stony patches, areas covered by dense understory and woody fuel accumulations were excluded from sampling. Metal frames (40 × 40 cm) were used to remove the monolith by inserting them into the ground up to 25 cm depth. Each monolith was segregated from the subjacent soil by introducing horizontally a metal plate at the bottom of the monolith. The extraction of the monoliths was made when their soil moisture was close to field capacity to facilitate their removal. Then monoliths were air-dried to get distinct levels of moisture (Table 1), monitored with TDR probes in a subset of them.

A subset of 24 randomly selected monoliths were assigned to be burned in semi-natural conditions in a burning bench of 300 cm length × 200 cm width × 50 cm depth, positioned at the outlet of a wind tunnel. The monoliths were placed on the bench in groups of six

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