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USING THERMOGRAVIMETRY AS A SIMPLE TOOL FOR NUTRIENT ASSESSMENT IN FIRE AFFECTED SOILS

SHORT TITLE: THERMOGRAVIMETRY FOR NUTRIENT ASSESSMENT IN BURNED SOILS

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ABSTRACT

Nutrient availability can be a limiting factor in the recovery of ecosystems after wildfire. Its evaluation is therefore critical for selecting appropriate restoration strategies in the post-fire period. This study explores, for the first time, the use of thermogravimetry (TG) as a rapid proxy for nutrient availability and soil recovery. Soil samples from five burned and unburned sites in Andisol of Tenerife (Spain) were selected to examine the medium-term impact of fire. Key soil chemical parameters (pH, EC, CEC, main cation and anions in the soil solution, TOC, TN and available P) were determined and TG performed. Burned soils showed significantly higher pH, Ca\(^{2+}\) and Mg\(^{2+}\) and a lower CEC, TOC and TN than the unburned counterparts and a site-dependent response for soluble SO\(_4^{2-}\) and available P was observed in the medium-term. Time elapsed since fire (8-10 months) could have masked additional fire-impacts. TG data allowed reasonable prediction of most soil properties and parameters, with \(r^2\) ranging from 0.4 to 0.9. The results demonstrate that the content of soluble nutrients is directly related to the amount of ash in the soil. The decrease of labile carboxyl-C was associated with an increase of pH and decrease of CEC, whereas the increase of recalcitrant and refractory pools was associated with the amount of TOC and TN. The results suggest that this novel application of an established method can provide, following an initial calibration step, rapid and inexpensive proxies for key parameters necessary for fire-induced ecosystem degradation and designing suitable restoration strategies in the post-fire period.

KEY-WORDS:

Wildfires, land degradation assessment, thermal analysis, soil chemical properties, Andisols.
INTRODUCTION

Wildfires can have profound effects on soil quality. Assessing the impacts of a fire on soil properties is an important step in determining the need and choice of specific ecosystem restoration treatments in the post-fire period (Bento-Goncalves et al., 2012). Several burn severity indexes (Moreno & Oechel, 1989; Ryan, 2002; Parsons et al., 2010) have been developed in order to classify fire impacts on key soil parameters presumed to directly influence ecosystem recovery and response in the post-fire period (Keeley, 2009). However, they generally focus on few specific variables (i.e. ground cover, soil structure and colour, ash colour and depth, soil water repellency, etc.) and are thus not particularly informative for predicting wider ecosystem responses (Jain et al., 2012; Keane et al., 2012).

The availability of nutrients is one key parameter that is often altered by fire impacts on soils and which affects ecosystem properties and functions (Pereira et al., 2016). For example, the ash produced during the combustion of aboveground fuels and soil organic matter (SOM) comprises charred organic residues and mineral components rich in nutrients (Bodi et al., 2014). As highlighted by Shakesby et al. (2016), the recognition of the key role of ash in the ecosystem response in the post-fire period has led to numerous studies in this field. The incorporation of these nutrients into the soil profile have been reported to lead to the ephemeral increase of the available and total nutrient content (see comprehensive reviews by Certini, 2005; Caon et al., 2014; Santín et al., 2015). Conversely, solute losses triggered by nutrient transport in the runoff and leaching thought the soil profile can reduce nutrient availability (Lasanta & Cerdà, 2005) and hinder vegetation recovery due to the limiting role of soil nutrients in plant productivity (Caon et al., 2014; Pereira et al., 2015). The analysis of nutrient levels in soil, however,
usually involves ??incl refs??, which is costly and time consuming and hence this important parameter is often not determined in post-fire assessments.

Thermogravimetry (TG), stand out as rapid, inexpensive and information-rich methodology, which has been used primarily characterizing SOM pools (Plante et al., 2009). It has also been proven useful as a simple proxy for other properties of different soils and land uses such as clay and carbonate content (Siewert, 2004) and was shown recently to also be effective as a proxy for physical and hydrological properties of fire-affected soils (Neris et al., 2014). However, to our knowledge, no studies exist that link TG data to soil chemical properties other than SOM after a forest fire.

The main aims of this study, therefore, were to evaluate the usefulness of TG for assessing fire impacts on SOM composition and to explore its potential links with other fundamental soil chemical properties related to soil nutrient availability and ecosystem recovery potential.

MATERIAL AND METHODS

Study region and characteristics of the forest fire

The volcanic island of Tenerife (Canary Islands, Spain) is situated between 27° 55’ and 28° 35’ N and between 16° 05’ and 16° 55’ W (Figure 1). The study area is located on the island’s northern hillsides (950 and 1,250 m a.s.l.). Where the annual precipitation range from 600 to 1,000 mm and is supplemented by up to 5 times the annual rainfall as water from condensation (Marzol, 2008). Basaltic pyroclasts and lava flows (0.7-0.01 M years old) with subsequent rejuvenations by analogous ashes (<0.01 M years old) are the main lithologies in the area, whereas pine forest (Pinus canariensis Chr. Sm. ex DC) and
Research design and sampling site selection

Five study sites were selected in the fire affected area (1-5; Figure 1) where previous studies provided information on the effects of fire on soil physical and hydrological properties (Neris et al., 2013) and the relationships between those properties and SOM characteristics (Neris et al., 2014). Each site consisted of a burned zone (B) and an unburned control zone (U) with the same soil type and pre-fire vegetation. The control zones had not been burned for at least 20 years. The elevation ranged from 900 to 1,200 m a.s.l. and the distance between U and B zones from 150 to 640 m. Firebreaks and ravines had been the main factors stopping the fire and protecting the U zones. Pine forest was the dominant vegetation, with some sites having undergrowth consisting of Erica sp and Morella faya (Aiton) Wilbur. The soils at all five sites were allophanic Andisols (Soil ...
Survey Staff, 1999), but with a wide range of pre-fire soil properties associated with regionally diverse forest soil characteristics (Table 1). The burn severity was classified as light for sites B1, B4 and B5, and moderate for zones B2 and B3, according to the metric by Ryan (2002). Due to sampling permission issues, soil samples were collected between 8 to 10 months after the fire. In this period, post-fire rainfall was 200-250 mm, although major soil erosion or deposition processes in the selected sites were unlikely due to the low intensity of the rainfall events before the soil sampling campaign. Given that this study aimed to evaluate TG as a proxy for key soil chemical parameters relevant to the recovery of fire affected ecosystems rather than immediate fire impacts on soil properties, this delay provided an excellent opportunity to carry out such an evaluation for a more stable, medium-term scenario that follows repeated post-fire wetting and drying cycles (Shakesby & Doerr, 2006) and ash redistribution (Bodi et al., 2014).

Soil sampling, preparation and analysis

For the purpose of this study soil samples previously obtained and analysed for physical and hydrological parameters by Neris et al. (2013) and for TA and specific SOM characteristics by Neris et al. (2014) were used. Briefly, three bulk soil samples were collected from the upper 5 cm of each burned and unburned site (3 samples x 10 sites). After collection, all the samples were air-dried and passed through a 2 mm sieve prior to analysis. A detailed explanation of the sampling design and methods is given in Neris et al. (2013).

For this study the following soil parameters were analyzed following standard methods (Soil Survey Staff, 1996): pH in H₂O at a soil:solution ratio of 1:2.5; electric conductivity (EC₁:₅) in a 1:5 soil:water extractant; cations and anions in the 1:5 suspension by atomic
absorption (Ca\(^{2+}\), Mg\(^{2+}\)), flame emission spectrophotometry (Na\(^+\) and K\(^+\)), turbidimetry after adding BaCl\(_2\) (SO\(_4\)^{2-}\)), brucine method (NO\(_3\)^- ) and Olsen method (PO\(_4\)^{3-}); cation exchange capacity (CEC) by ammonium acetate (NH\(_4\))OAc); available phosphorus (P) by Olsen method; and total C and N (TN) by dry combustion. As the samples did not contain inorganic carbonates (Neris et al., 2013), total C determined was taken as representing soil Total Organic Carbon (TOC).

In order to evaluate links between the medium-term impact of the fire on SOM composition and soil chemical characteristics the data on chemical properties obtained for this study was correlated to TG data previously obtained by Neris et al. (2014). In summary, thermogravimetry (TG) and differential thermal analysis (DTA) were performed in a simultaneous thermal analyser. Thermograms were obtained by heating the soil sample at 10 °C min\(^{-1}\) from 30 to 700 °C under O\(_2\) flux (20 cm\(^3\) min\(^{-1}\)). Weight losses for each 10 °C temperature range (30 to 700 °C) were determined according to Siewert (2004). DTG and DTA obtained previously showed the typical thermo-oxidative decay comprising 4 main steps (De la Rosa et al., 2008a; Merino et al., 2014): (i) dehydration processes from 30 to 200 °C (Endo0), (ii) exothermic oxidation of thermolabile compounds from 200 to 380 °C (Exo1), (iii) exothermic oxidation of recalcitrant compounds from 380 to 475 °C (Exo2), and (iv) exothermic oxidation of refractory compounds from 475 to 700 °C (Exo3). As reported by Neris et al. (2014) for the soils examined in this study, burned soils presented lower values of total weight loss (TWL) from 30 to 700 °C and weight loss (WL) from 200 to 700 °C, indicative of a partial consumption of organic compounds by fire. Additionally, the labile organic matter pool (Exo1) of burned soils was significantly lower than that of the unburned counterparts, whereas recalcitrant (Exo2) and refractory (Exo3) organic matter pools were significantly
higher in burned soils. Sites 1 and 3 and, to a lesser extent 2, showed the more notable changes in TWL, WL and organic pools distribution. A detailed explanation of the TA methods and results is given in Neris et al. (2014).

Statistics

SPSS version 17.0.0 was used for the statistical analysis of the results. Data were analyzed for normality using the Shapiro-Wilk test and transformed (Box-Cox) as necessary at all sites. Two-way analysis of variance (ANOVA) was used to study the significant effect of soil type (site) and fire (site × fire) on the chemical parameters evaluated. Correlations between soil chemical properties (dependent variables) and weight losses at different temperature range intervals (independent variable) were examined for the burned soils by Pearson-r correlation and simple linear regression respectively. A significance level of 0.05 was chosen (p < 0.05).

RESULTS

Pre-fire soil chemical properties and medium-term fire impacts

Soil characteristics and significant statistical differences for the study sites are given in Table 1. The unburned soils (U zones) exhibited a pH from moderately acid to neutral and EC_{1:5} ranging from 125 to 655 µS cm^{-1}. NO₃⁻, SO₄^{2-}, Na⁺ and Ca^{2+} were the main ions in the soil solution. Both TOC and TN showed high values in comparison with other soil types, ranging from 72 to 174 and 3.5 to 11.6 g kg^{-1} respectively. Average CEC was 28.7 ± 7.0 cmol_c kg^{-1}. Zones U1 and U3 showed the highest values of EC_{1:5}, cations, anions, TOC, TN and CEC and lowest pH. Significant statistical differences between the 5 sites studied were found for all the chemical properties evaluated except for PO₄^{3-} (Table 2). However, since the magnitude of these differences is low and all the soils were classified...
as allophanic Andisols, these differences were considered trivial and no major effects on
the soil response to fire can be expected from them.

The burned soils exhibited a statistically significant lower TOC and TN contents, whereas
P differences depended on the site evaluated (site × fire interaction was statistically
significant) (Tables 1 and 2). Available P values were larger for burned than for unburned
soils at sites 1 and 3 but lower at sites 2 and 5. Burned zones also exhibited significantly
higher pH values (from 6.3 ± 0.5 to 6.7 ± 0.5). The largest differences between burned
and unburned soils regarding TOC, TN and pH were found in sites 1, 2 and 3, whereas
those differences were minor or non-existent in sites 4 and 5. The values of CEC were
significantly lower and Ca^{2+} and Mg^{2+} content was significantly higher in burned zones
in comparison to their unburned counterparts. This response was observed mainly in sites
1 and 3, whereas it was minor in sites 2, 4 and 5 (CEC was slightly higher in B4 than U4).
None of the anions evaluated showed statistically significant differences between
unburned and burned zones, although the differences between burned and unburned zones
regarding SO_{4}^{2-} depended on the site evaluated (site x fire interaction was statistically
significant). Zones B1 and B2 showed lower SO_{4}^{2-} in comparison with their unburned
counterparts, whereas zone B3 showed noticeably higher values than U3 and these
differences were negligible in sites 4 and 5.

Using TG to predict soil chemical properties of fire-affected soils

Soil chemical properties analysed for this study were evaluated for correlations with the
different indexes of SOM content and composition: (i) the general TG thermo-oxidative
step parameters (Exo1, 2 and 3), and (ii) the indexes associated to the weight losses for
each 10 °C temperature range obtained by TG. Thermo-oxidative steps were not
correlated to 4 of the 15 properties evaluated, including key parameters such as pH, most anions (SO₄²⁻, PO₄³⁻) and P (Table 3). The simple linear regressions performed showed that the association were weak with properties such as CEC, K⁺, TOC or TN (r² < 0.5), moderate with properties such as EC₁:₅, NO₃⁻, ∑anions₁:₅ or Na⁺ (0.5 < r² < 0.7) and relatively strong with Ca²⁺, Mg²⁺ or cations (r² > 0.7) (Table 3). The weight losses at the recalcitrant pool (Exo2) showed the highest values of r², explaining over 80% of the variability of some key parameters (i.e. EC₁:₅, Ca²⁺ and Mg²⁺). Weight losses at the labile pool (Exo1) explained less than 80% of the variability of some parameters evaluated. The refractory pool (Exo3) was only associated with CEC, explaining 57% of the variability of this parameter. The slopes of the regressions lines between soil properties and thermos-oxidative steps were negative for Exo1 except with CEC, positive for Exo2 and negative for Exo3 (Table 3).

In contrast, the 10 °C temperature range steps calculated correlated to all the parameters evaluated except PO₄³⁻ (Table 3). In addition, higher r² than conventional thermo-oxidative steps were observed for all the parameters using this approach (r² was equal for K⁺). Weight losses at 10 °C temperature range steps explained less than 50% of the sample variability of 3 parameters (SO₄²⁻, K⁺ and P), between 50 and 70% of 2 (pH and CEC), and more than 70% of 9 parameters evaluated (EC₁:₅, NO₃⁻, ∑anions₁:₅, Ca²⁺, Mg²⁺, Na⁺, ∑cations₁:₅, TN and TOC) (Table 3). Over 90% of the variability of TOC was explained. Weight losses at 10 °C steps at the range 370-560 °C, corresponding to the recalcitrant pool (Exo2) and the less stable compounds of the refractory pool (Exo3), showed the larger number of statistically significant correlations and the strongest associations to the parameters evaluated (see Figures 2 and 3). Soil parameters such as EC₁:₅, Ca²⁺, Mg²⁺, Na⁺, K⁺, ∑cations₁:₅, NO₃⁻, TN or TOC presented their highest Pearson-r values with 10
8°C steps at this temperature range. The maximum coefficient of determination ($r^2$) for most of these parameters is in the range 490-520 °C, except for TOC and TN (400-410 and 460-470 °C respectively) (Table 3). $SO_4^{2-}$ and CEC also showed secondary peaks of Pearson-r values at this temperature range. The correlation between all the parameters stated above and the weight losses at 10 °C steps for this range (370-560 °C) were positive (Figures 2 and 3). Other parameters such as pH, CEC, $SO_4^{2-}$ or P showed their maximum Pearson-r and $r^2$ values at the range 150-340 °C (Table 3 and Figures 2 and 3). This temperature range corresponds to the less thermally stable compounds of the labile pool (Exo1) and, marginally, to the more thermally stable ones of the Endo0. The Pearson-r values in this temperature range were positive for EC and $SO_4^{2-}$, whereas pH and P showed negative values (Figures 2 and 3). Two marginal peaks of Pearson-r values where observed at the temperature ranges: i) 40-120 °C, corresponding to the dehydration step, for CEC and TOC (positive correlations) and P and pH (negative correlations), and ii) 610-650 °C, corresponding to the refractory pool (Exo3), for pH, EC$_{1:5}$, $SO_4^{2-}$, $NO_3^-$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $\sum$ cations$_{1:5}$, CEC and P (all positive except CEC) (Figures 2 and 3). None of the last soil parameters showed maximum values of $r^2$ at this temperature range.

DISCUSSION

Medium-term impact of fire on soil chemical properties

Eight to ten months after the fire, several fire impacts widely reported from other environments and summarised in the reviews by Certini (2005) and Santín & Doerr (2016) were also significant in the study area. They comprised a decrease of TOC, TN and CEC, an alteration of the chemical composition of the soil organic compounds and an increase of pH and key cations ($Ca^{2+}$, $Mg^{2+}$) and some anions ($SO_4^{2-}$) in the soil solution. As widely reported (e.g. Giovannini et al., 1990; Gónzalez-Pérez et al., 2004),
the impact of heating on SOM directly affects TOC and TN content and chemical composition of C and N forms, which are reduced and become more recalcitrant in the soil surface (Aznar et al., 2016). This impact has been detected by other researchers also in the medium- and longer-term (e.g. Kutiel & Inbar, 1993; Johnson et al., 2007; Mora et al., 2016).

It is suggested that the largest reduction and chemical alteration of SOM of sites B1 and B3 led to: i) a decrease of CEC since SOM show high density of surface charge that contribute to soil cation adsorption (Giovannini et al., 1990; Certini, 2005; Inbar et al., 2014); ii) an increase of cations in the soil solution as a consequence of their release during the mineralization of organic compounds (Pereira et al., 2014; Wang et al., 2016); and iii) an increase of pH due to the stated rise of alkaline salts and denaturation of organic acids (Kutiel & Naveh, 1987; Aznar et al., 2016) in these sites. The direct association between SOM and CEC is also highlighted by the high correlation coefficient between both properties for the soils studied (Pearson-r = 0.67; data not shown). Contrarily, where SOM showed smaller differences between burned and unburned sites (B2, B4 and B5), no major changes in CEC, pH or cations were observed, as it was previously reported by Mora et al. (2016) studying fire-affected pine forest form volcanic areas. However, it is also likely that these effects could have been covered up in the remaining sites (B2, B4 and B5) by hydrological and biogeochemical processes occurred in the post-fire period (8-10 months) due to the transient nature of these fire impacts (Bodi et al., 2014; Pereira et al., 2015).

The comparison of burned and unburned soil properties suggests also that some of the immediate impacts of fire on soil properties could have been diluted in the medium-term.
Often reported immediate impacts of severe fires on soils, such as the increase of certain nutrients (available P, anions and Na\(^+\) and K\(^+\)) and soil EC (Iglesias et al., 1997; Certini, 2005; Dorta Almenar et al., 2015), were not observed in this study. The absence of differences in these parameters for the studied soils could be attributed to: i) time elapsed since fire and the hydrological and biological processes occurring in this interval, and ii) specific anion sorption of Andisols. The occurrence of major erosion or deposition events inducing extensive soil redistribution processes in the selected areas is unlikely due to the low rainfall intensity of the events that occurred before soil sampling (max. daily precipitation: 39 mm day\(^{-1}\)) and the moderate infiltration rate of the study areas (ranging from 18 to 33 mm h\(^{-1}\)) reported by Neris et al. (2013). However, infiltration processes and minor saturated overland flow events were likely during these rainfall events (200-250 mm in 8-10 months). These low-intensity events could have caused some ash redistribution, and selective solute leaching (Lasanta & Cerdà, 2005; Cancelo-Gonzalez et al., 2013), masking the effect of fire on nutrient availability in the medium-term (Pereira et al., 2015). Therefore, the initial concentration peak of monovalent cations (Na\(^+\) and K\(^+\)) and NO\(_3\)\(^-\) reported in numerous studies could have been counteracted by selective solute leaching during the rainfall events due to the higher mobility of these nutrients in comparison to other ions (Couto-Vazquez & Gonzalez-Prieto, 2006; Dorta Almenar et al., 2015). In addition, the release of PO\(_4\)\(^{3-}\) and SO\(_4\)\(^{2-}\) during the combustion of organic compounds is likely to have had little impact on their concentration in the soil solution of Andisols due to the specific sorption of those anions to the chemically reactive surfaces present in this soil type (Rajan, 1978; Dorta Almenar et al., 2015). According to Strahm & Harrison (2007) the sorption capacity of a soil is specific of the anion considered and follows the order: PO\(_4\)\(^{3-}\) > SO\(_4\)\(^{2-}\) > NO\(_3\)\(^-\), being specific for PO\(_4\)\(^{3-}\), partially specific for SO\(_4\)\(^{2-}\) and non-specific for NO\(_3\)\(^-\). Consequently, andic constituents can buffer the input of
PO_4^{3-} and, marginally, SO_4^{2-} from the ash through specific sorption to the soil colloids and mask the effect of fire, whereas their impact on NO_3^- is limited.

These results suggest that the temporal evolution of the fire-impacts on chemical properties is influenced by: i) the initial degree of mineralization and volatilization of SOM compounds that lead to their decrease, and also major changes in its chemical structure; ii) the initial release of nutrients from the oxidation of SOM; and iii) the alteration of the hydrological response of the ecosystem that controls ash and nutrient transport by leaching, dilution in the runoff and erosion processes in the medium-term. The interaction of all these factors can lead to a high level of variability regarding key soil chemical properties related to the ecosystem recovery and, thus, to several post-fire scenarios that should be evaluated independently when designing suitable post-fire restoration treatments. Methods to rapidly screen key soil properties in the post-fire period are, therefore, necessary to design appropriate recovery plans.

Linking soil chemical properties to SOM pools

The soil chemical properties evaluated here showed, in general, strong association with the TG results. Neris *et al.* (2014) already suggested the suitability of TG as a simple proxy for fire impacts on soil physical and hydrological properties of volcanic soils, whereas Siewert (2004) used TG to rapidly screen key soil properties such as SOM, clay and carbonate content of different soil types and land uses. However, to our knowledge, this is the first study on fire-affected soils that links TG data to soil chemical properties other than SOM. The results obtained here therefore break the ground for developing a rapid proxy for key soil chemical properties from fire-induced medium-term changes in the thermal stability of SOM (TG results).
The results demonstrate that the content of the recalcitrant (in the temperature range 375-550 °C) and, mainly, the refractory pools (in the range 620-640 °C) are directly related to the content of EC\textsubscript{1:5}, pH, P, cations and some anions (SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}-) in the soil solution. De la Rosa \textit{et al.} (2008b) have suggested that weight losses at the refractory pool correspond mainly to charred organic residues whereas Santin \textit{et al.} (2016) reported that the production of pyrogenic OM has its maximum at temperatures over 600 °C. Several studies have previously suggested a direct impact of ash on soil nutrient content, basing this hypothesis on laboratory or field leaching experiments (Marion \textit{et al.}, 1991; Molina \textit{et al.}, 2007; Escudey \textit{et al.}, 2015) or studies of ash composition (Khanna \textit{et al.}, 1994; Pereira \textit{et al.}, 2014; Santin \textit{et al.}, 2015) and post-fire soil nutrient content (Khanna & Raison, 1986; Andreu \textit{et al.}, 1996; Dorta Almenar \textit{et al.}, 2015). However, unlike these previous studies, we demonstrate a direct quantitative link between the content of charred organic residues in the soil (represented by the SOM refractory pool) and soil nutrient values using a field approach and samples affected by a wildfire.

The absence of correlations for PO\textsubscript{4}\textsuperscript{3-} and the weak association shown by SO\textsubscript{4}\textsuperscript{2-} and P can be attributed to the specific adsorption of these anions (Barrow, 1985) to the reactive surface of Andisols as suggested by Dorta Almenar \textit{et al.} (2015). This buffering effect on their concentration in the soil solution may mask their expected response to fire and, thus, interfere with the regressions developed. Additionally, the time since the fire (the sampling campaign was carried out 8-10 months after the fire) and the hydrological and biogeochemical processes occurring in this interval, could have diluted some of the immediate effects of fire on key properties. Therefore, stronger associations between TG data and those nutrients could be expected, for example, for samples collected...
immediately after the fire and for soil types in which this buffering effect is not present. It is also notable that all the soluble cations (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^+\), K\(^+\)), non-specifically-adsorbed anions (NO\(_3^-\)) and EC\(_{1:5}\) showed the strongest association to TG data in the temperature range 500-520 °C. Additionally, all of them, together with P, shared a correlation peak at 620-640 °C (Figures 2 and 3). Further studies are needed to determine the compounds responsible for these associations and therefore for the nutrients increase in the post-fire period.

The labile pool showed strong correlations with key properties such as pH (negative) and CEC (positive). It has been reported that the increase of pH after a fire can be related, also to the increase in alkaline salts of the main cations, due to organic acid denaturation (Kutiel & Naveh, 1987; Aznar et al., 2016). Those organic acids include carboxyl and aliphatic C, which are thermally labile organic compounds correspondent to the labile pool (Exo1) (Lopez-Capel et al., 2005; Marinari et al., 2010). Regarding CEC, according to Kaiser et al. (2008), the contribution of SOM to CEC can be attributed mainly to the negatively charged sites present in carboxyl C, again one of the main components of the thermally labile pool (Exo1) (Lopez-Capel et al., 2005; Marinari et al., 2010). Therefore, a fire-induced reduction in labile carboxyl and aliphatic C may lead to an increase in pH and a decrease in CEC in the post-fire period. In addition, it is suggested that the direct correlation found between Endo0 and CEC can be related to the direct association between CEC and clay and amorphous minerals typical of volcanic soils. As suggested by Neris et al. (2014), Endo0 of air dried soils corresponds to evaporation of water retained at high tensions (clay-controlled microporosity) and CEC depends on the negatively charged sites of clay and clay-like minerals (Kaiser et al., 2008).
TOC and TN of the burned soils evaluated were mainly associated with the recalcitrant pool, whereas the refractory pool also showed lesser correlation for both parameters and the labile pool for TOC. This stronger correlation of TOC and TN with the recalcitrant pool than to the other SOM pools is suggested to be due to the higher recalcitrance of the SOM of the burned soils a consequence of the forest fire, as reported by Neris et al. (2014). Actually, the correlations between TG data and TOC and TN for the unburned soils evaluated showed that the degree of correlation was higher and more homogeneous along the three organic pools (data not shown), probably due to the higher amount of organic compounds and more homogeneous distribution along the three pools.

TG as a proxy for key soil chemical properties in the post-fire period: implications and prospect.

The evaluation of the fire impacts on soil properties is an essential step for land managers in assessing accurately the ecosystem condition in view of selecting the most appropriate restoration approach. For the vegetation and soil microbiota restoration it is important to evaluate the nutrient availability and its temporal distribution in the post-fire period since nutrients can be limiting factors for their recovery (Caon et al., 2014). Several drivers such as burn severity, fire recurrence and time since fire affect fire impacts on soil properties. Also, environmental factors such as topography, rainfall pattern, vegetation type, litter thickness, soil type, soil moisture, can lead to different post-fire scenarios in terms of nutrient availability. This diversity of factors and drivers limits the accuracy of the fire impacts prediction from simple burn severity metrics and, therefore, a series of different soil analysis, which tend to be expensive and time-consuming, are usually needed to evaluate each post-fire scenario. As an alternative approach, the results obtained in this study suggest that thermal analysis can be used as a rapid and inexpensive
predictor of key soil chemical parameters involved in the ecosystem recovery even
several months after the fire. A single calibration step to initially link TG data to site-
specific key soil chemical properties evaluated using conventional methods from new or
existing datasets is needed. However, once this initial relationship is established, simple
regressions allow investigators to predict nutrient availability with a reasonable level of
accuracy. Thus, it is suggested that this methodology is particularly useful for assisting
land managers to select adequate post-fire restoration actions by providing rapid and
inexpensive information on critical variables in post-fire ecosystem recovery potential:
nutrient availability and its spatial and temporal distribution.

CONCLUSIONS

This study examined, for the first time, the use of thermogravimetry (TG) as a proxy for
the impacts of fire on nutrient availability. This was done by examining the medium-term
effect of a wildfire (8-10 months post-fire) on Andisols and their link to SOM
composition using TG. Several soil chemical parameters that are critical in determining
ecosystem recovery potential, mainly the concentration of basic cations, TOC or TN, were
affected by the fire in the medium-term. However, widely reported fire impacts were not
found here probably due to their ephemeral effect and the specific response of Andisols
to the increase of some anions and their specific sorption to the short-range order
compounds.

The associations found between key soil parameters of burned soils and TG data at
specific temperature ranges highlight the influence of specific SOM pools on nutrient
availability and other chemical parameters involved in ecosystem recovery in the post-
fire period. These are: i) an increase of the thermal stability and recalcitrance of the
organic C- and N-forms, ii) a direct quantitative effect of ash content on soluble nutrients
in the soil solution, and iii) the importance of labile organic compounds on key properties such as pH or CEC. Additionally, these strong associations enable using TG as predictor of nutrient availability and key chemical parameters in the medium-term of a post-fire ecosystem. The results of this study suggest that this novel application of an established method can provide, following an initial calibration step, a rapid and inexpensive proxies for key soil parameters relevant for assessing fire-induced ecosystem degradation, which in turn allows implementing the most effective restoration strategies in the post-fire period.

ACKNOWLEDGEMENTS

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REFERENCES


thermal analysis to monitor C and N changes in soil organic matter from a Mediterranean fire affected forest. Catena 74: 296-303. DOI: 10.1016/j.catena.2008.03.004


Johnson, D, Murphy, JD, Walker, RF, Glass, DW, Miller, WW. 2007. Wildfire effects on forest carbon and nutrient budgets. Ecological Engineering 31: 183-192. DOI: 10.1016/j.ecoleng.2007.03.003


Santín, C, Doerr, SH, Otero, XL, Chafer, CJ. 2015. *Quantity, composition and water contamination potential of ash produced under different wildfire severities.* Environmental Research 142: 297-308. DOI: 10.1016/j.envres.2015.06.041


Table 1: Key chemical parameters for unburned (U) and burned (B) soils per zone. Mean and standard deviation (SD) of pH, cation exchange capacity (CEC – cmolc kg⁻¹), soil salinity (EC1:5 - µScm⁻¹), main anions and cations in the soil solution (mmolc l⁻¹), total organic carbon (TOC- g kg⁻¹), total nitrogen (TN - g kg⁻¹) and available P (P – mg kg⁻¹) were calculated (n=3). ∑anions1:5 value does not include Cl⁻ nor alkalinity.

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<th>B</th>
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<th>B</th>
<th>U</th>
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Table 2: Significance of effect of site, fire and site x fire on key chemical soil parameters. Two-way ANOVA (site x fire; n=30) for pH, cation exchange capacity (CEC), soil salinity (EC1:5), main anions and cations in the soil solution, total organic carbon (TOC), total nitrogen (TN) and available P (P) were evaluated (*: significant at p < 0.05).

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<th>Site x Fire</th>
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<td>0.244</td>
</tr>
<tr>
<td>CEC</td>
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<td>0.004*</td>
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<tr>
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<td>0.000*</td>
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<td>NO3⁻</td>
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<td>Mg²⁺</td>
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<tr>
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Table 3: Regression parameters for key chemical soil parameters and the typical thermo-oxidative steps (Exo1, Exo2 and Exo3) and 10 °C temperature range steps. $r^2$ for pH, soil salinity (EC1:5), cation exchange capacity (CEC), main anions and cations in the soil solution, total organic carbon (TOC), total nitrogen (TN) and available P (P) were calculated. Data transformed as necessary (Box-Cox). Temperature range (°C) for the maximum $r^2$ and regression equation ($y = \beta x + \epsilon$) were calculated for the 10 °C temperature range steps.

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<th>Exo1</th>
<th>Exo2</th>
<th>Exo3</th>
<th>10 °C temperature range steps</th>
<th>$r^2$</th>
<th>Regression equation</th>
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<td>(EC1:5)$^{-1}$</td>
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<td>510-520</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(NO$_3^{-}$)$^{-1}$</td>
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<td>Ln(Mg$_{2+}$)</td>
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<td>(TN)$^{1/2}$</td>
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<td>-</td>
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