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Paper:

Neris, J., Doerr, S., Tejedor, M., Jiménez, C. & Hernández-Moreno, J. (2014). Thermal analysis as a predictor for hydrological parameters of fire-affected soils. *Geoderma*, 235-236, 240-249.

<http://dx.doi.org/10.1016/j.geoderma.2014.07.018>

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Thermal analysis as a predictor for hydrological parameters of fire-affected soils

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This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi:10.1016/j.geoderma.2014.07.018.

Abstract

Soil burn severity indexes have been developed to rapidly assess ecosystem damage from vegetation fires and predict associated risks during the post-fire period. In terms of the hydrological impacts, the lack of measurable relationships between the commonly determined metrics and post-fire hydrological responses has limited their potential to predict and mitigate post-fire hazards. This study examines the link between post-fire organic matter characteristics and main soil physical and hydrological properties (clay content, bulk density, aggregate stability, water retention, water repellency, rainfall-runoff ratio and sediment concentration in runoff) in order to explore the potential use of organic matter characteristics as a proxy for the soil property-related hydrological impacts of fire. Soil samples from five fire-affected burned and unburned control sites in Andisols areas of Tenerife (Canary Islands, Spain), previously studied for hydrological processes, were selected and thermogravimetric analysis (TG) carried out to evaluate fire impacts on their organic matter composition. TG data were used to perform simple linear regressions with hydrological soil properties obtained previously. Organic matter composition showed noticeable homogeneity among the unburned sites, despite substantial within and between site variability for most properties, which may simplify soil burn severity assessment. Fire led to a decrease in the relative amount of the labile organic matter pool and an increase in the recalcitrant and/or refractory pool depending on study site. TG data, using 10 °C temperature range steps, allowed reasonable prediction of most soil properties and parameters, with R^2 ranging from 0.4 to 0.9 and with $R^2 \geq 0.6$ for 6 of the 8 parameters evaluated. The labile pool and the dehydration range affected positively bulk density, aggregate stability, wilting point and water repellency and negatively field capacity and sediment concentration, whereas the

refractory pool showed the opposite trend. The recalcitrant pool was unrelated to other soil properties except clay content and runoff. These results, in conjunction with the simplicity of the TG analysis suggest that, after an initial calibration step to link TG data to the site-specific post-fire soil properties, this method may be a useful tool to allow rapid and cost-effective evaluation of soil burn severity and anticipated soil hydrological response after the fire.

Keywords: *Wildfires, thermogravimetry, soil physical properties, hydrological response, Andisols, soil burn severity.*

1. Introduction

Post-fire assessments of burned terrain are commonly performed to identify risks to lives, properties and natural or cultural resources by evaluating indirectly the impact of fire on ecosystem dynamics (Parsons et al., 2010). Soil burn severity indexes, which classify fire-related changes of key parameters presumed to directly influence the post-fire ecosystem response (Keeley, 2009), have been developed for this purpose. However, despite their practical usefulness and importance both in fire research and management, some limitations exist regarding (i) their measurement and (ii) their link with the ecological response (Keane et al., 2012; Moody et al., 2013).

From a hydrological perspective a major limitation has been the often poor connection between the soil burn severity indexes and the ecosystem responses in terms of runoff and erosion as highlighted in a comprehensive review of the subject by Moody et al. (2013). This limits the usefulness of these indexes in predicting post-fire hydrological behaviour and Moody et al. (2013) argue that progress requires (i) direct links to be

established between the soil burn severity indexes and soil properties related to runoff and erosion, and (ii) these to be included into soil erosion prediction models.

Thermal analysis (TA) techniques, as for example thermogravimetry (TG), have been increasingly used to characterize the soil organic matter (SOM) pools as a rapid, inexpensive and information-rich procedure (Plante et al., 2009). TA has proved its usefulness to evaluate SOM quantity and composition (Fernandez et al., 2011) both in unburned (see e.g. Schulten and Leinweber, 1999; Siewert, 2004) and burned soils (see e.g. De la Rosa et al., 2008a; Duguay and Rovira, 2010). Due to the noticeable impact of fire on SOM (Certini, 2005; González-Pérez et al., 2004) and the strong influence of SOM on infiltration (Lado et al., 2004; Tejedor et al., 2013) and runoff and erosion related soil properties such as structure (Giovannini and Lucchesi, 1983; Mataix-Solera et al., 2011), water repellency (Doerr et al., 2000; Martínez Zavala et al., 2009) or water storage capacity (Boix-Fayos, 1997; Stoof et al., 2010), TA may also have promise to act as predictor of soil burn severity and hydrological response. It allows rapid determination of the fire impacts on the SOM and might also enable prediction of other related soil properties relevant to post-fire runoff and erosion dynamics.

The main aim of the work presented here was therefore to evaluate the usefulness of TA to assess fire impacts on soil organic matter composition and explore its potential links with other fundamental soil properties related to the post-fire runoff and erosion response.

2. Methodology

2.1 Study region

The volcanic island of Tenerife (Canary Islands, Spain), with a total size of 2,057 km² and a maximum elevation of 3,718 m a.s.l., is situated between 27° 55' and 28° 35' N and between 16° 05' and 16° 55' W (Figure 1). The study zone is located on the island's northern hillsides, between 950 and 1,250 m a.s.l., where the average annual precipitation of 600-1,000 mm is supplemented by water from condensation, resulting in up to 5 times the annual rainfall (Marzol Jaén, 2005). Bedrock consists of basaltic pyroclasts and lava flows (0.7-0.01 M years) with subsequent rejuvenations by analogous ashes (<0.01 M years). The vegetation is mainly pine (*Pinus canariensis*) and rainforest (*Laurus novocanariensis*, *Appollonias barbujana*, *Persea indica*, *Ilex canariensis*, *Morella faya*, *Erica scoparia* and *Erica arborea*, among other species). The soils are mostly allophanic Andisols and are classified as Ustands and Udands depending on their soil moisture regime (Soil Survey Staff, 1999). Although occupying much smaller areas, soils of the Inceptisol and Entisol orders (Soil Survey Staff, 1999) are also found.

2.2 Characteristics of the forest fire

A forest fire on 30 July 2007 burned an area of almost 17,000 ha with a perimeter of 90 km (Figure 1) (Instituto Canario de Estadística, 2013). The fire occurred during high temperatures (30-45 °C), low relative humidity (5-10 %) and winds occasionally exceeding 50 km h⁻¹. The fire covered a large elevation range (500-2,000 m a.s.l.) with moderately-steep hillslopes (10 to 25°) and different types of vegetation. Woodland was the main vegetation type affected (13,500 ha), the majority of which consisted of pine forest (95%) and the remainder rainforest.

2.3 Research design and sampling site selection

For this study, TA and other specific analysis (see 2.5 section) were performed on samples previously obtained and analysed for general soil properties by Neris et al. (2013a). The new data obtained here was compared with data produced in this previous work in order to evaluate links between the fire impact on SOM composition and hydrologically relevant soil properties. Five study sites had been 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., 2013a). 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 Fayal-Brezal (*Erica sp* and *Morella faya*). The soils in all five sites were allophanic Andisols (Soil Survey Staff, 1999), but with a wide range of pre-fire soil properties to encompass regionally diverse forest soil characteristics (Table 1). Burn severity was classified as light for sites B1, B4 and B5 and moderate for zones B2 and B3 according to the metric of Ryan (2002) based on the visual evaluation of the vegetation and SOM consumption. Due to access permission issues, soil samples were collected between 8 to 10 months after the fire. In this period, post-fire rainfall was around 250 mm. This allowed for the redistribution of the ash cover, repeated wetting and drying cycles and some ground vegetation recovery. Given that the immediate post-fire characteristics often undergo rapid changes related to wetting and drying events (Shakesby and Doerr, 2006) and the redistribution of ash (Bodí et al., 2014), this gave the opportunity to evaluate the more stable, medium-term impacts of fire in this region.

2.5 Soil sampling, preparation and analysis

For the purpose of this study soil samples analysed previously for physical and hydrological parameters by Neris et al. (2013a) were used to perform TA and specific SOM analysis. Three bulk soil samples had been collected from the upper 5 cm of each burned and unburned site. All the samples had been air-dried and passed through a 2 mm sieve prior to analysis.

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed in a simultaneous thermal analyser (Perkin Elmer; STA 6000). Thermograms were obtained by heating approximately 15 mg of ground soil sample in an alumina crucible at 10 °C min⁻¹ from 30 to 700 °C under O₂ flux (20 cm³ min⁻¹). The derivative of the TG curve (DTG) was calculated to facilitate interpretation of the thermal events. According to the terminology of Dell'Abate et al. (2002) total weight loss (ExoTot) associated with the decomposition of the SOM (200-700 °C) as well as the ratios between the weight loss at the first (Exo1), second (Exo2) and third (Exo3) exothermic reactions and the ExoTot were calculated. Weight losses for each 10 °C temperature range (30 to 700 °C) were determined. Total C analysis was performed using a CNHS Flash EA 1112 Elemental Analyzer. As the samples did not contain inorganic carbonates, C estimated was assumed to be soil Total Organic Carbon (TOC).

Other complementary physical and hydrological properties had been evaluated in previous studies and a detailed explanation of the methods used is given in Neris et al. (2013a). Briefly, bulk density (BD) was measured on an oven-dried weight basis of a core sample (Blake and Hartge, 1986). Texture was determined using the Bouyoucos

densimeter method following a H₂O₂ treatment (Gee and Bauder, 1986). Water retention at field capacity (FC: 33kPa) and permanent wilting point (WP: 1500 kPa) were determined by Richard's pressure plates (Klute, 1986). Aggregate stability (AS) was determined by wet-sieving on a 0.2 mm sieve (Bartoli et al., 1991). Water Drop Penetration Time test (WDPT) was used to determine water repellency (Doerr, 1998). Infiltration, runoff and soil loss at plot scale were studied using a rainfall simulator (Nacci and Pla, 1991) (60 mm h⁻¹ during 35 minutes over a 0,1 m² area) to calculate the runoff-rainfall ratio (RR: %) and the sediment concentration in the runoff (SC: g L⁻¹).

2.6 Statistical analysis

SPSS version 17.0.0. was used for the statistical analysis of the results. Data were analyzed for normality and transformed (Box-Cox) as necessary for statistical analysis at all sites. The relationship between soil properties (dependent variables) and weight losses at different temperature range intervals (independent variable) was examined by Pearson-r correlation and simple linear regression.

3. Results

3.1 Soil characteristics

Soil characteristics for the study sites are given in Table 1. In accordance with their classification as Andisols, all the unburned soils contained considerable quantities of TOC (on average 11.6%), although substantial within and between site variability is evident. TOC exceeded 15% in zones U1 and U3, and ranged 7 to 9.5% in zones U2, U4 and U5. The unburned zones showed a moderate clay content varying from 13 to 21% and low BD with minimums barely reaching 0.5 Mg m⁻¹ and maxima getting close to the limit for Andisols, 0.9 Mg m⁻¹. In general, AS, WDPT and water retention

capacity at both FC and WP were high, but also varied between sites. FC ranged from 47 to 75 % whereas WP varied from 17 to 29%. According to their soil water repellency values, soils were classified as extremely (U1 and U2) and slightly water repellent (U4), while AS ranged from 29 to 48%.

TOC was reduced in most of the burned zones. The highest variations in TOC were observed within sites 1 and 2, whereas sites 3 and 5 showed slight reductions and no change were observed at site 4. Most other soil properties related to hydrological behaviour such as BD, AS and WDPT also showed a general trend of reduced values after the fire. BD reached values close to 0.5 Mg m^{-1} after the fire, decreasing for unburned sites with higher values, and remaining unchanged where they already presented similar values (sites 1 and 2). AS decreased mainly in zone B1, B3, but also in B4. WDPT decreased considerably at the sites with the highest pre-fire levels (zones B1, B2 and, at a lesser extent, in B3). In contrast, water retention capacity was inconsistently affected. FC increased at sites 1 and 3, decreased in sites 2 and 4, and remained constant at site 5. WP showed only slight changes after the fire.

3.2 Soil characterization using TG

DTG and DTA thermograms obtained for the unburned soils (Figure 2) showed a thermo-oxidative decay with four main steps: (i) endothermic dehydration with maximum at $86 \text{ }^\circ\text{C}$ (Endo0), (ii) exothermic reaction with maximum at $329.0 \text{ }^\circ\text{C}$ (Exo1), (iii) exothermic reaction with maximum at $388 \text{ }^\circ\text{C}$ (Exo2), and (iv) exothermic reaction with a maximum at $476 \text{ }^\circ\text{C}$ (Exo3).

For unburned soils, the mean weight loss from 30 to 700 °C (TWL), including dehydration, SOM degradation and decomposition of minerals was 28% (Table 2). This value was reduced to 22% when the dehydration processes was excluded (200 to 700 °C - ExoTot). The regression between TOC and ExoTot showed a close relation between these parameters (Figure 3). This result allowed evaluating the contribution of both the soil mineral and the organic phase to the TG. According to the equation obtained, in absence of TOC ($x = 0$), there was still a weight loss of 2% through this temperature range, which could be attributed to thermally unstable minerals. This result highlights the limited contribution of the mineral phase to the weight loss in these soils. In addition, a high weight loss can be observed at the dehydration step (Endo0) in unburned plots. Endo0 was found to be directly correlated with the air-dried sample water content (data not shown in tables: Pearson-r: 0.925; $p < 0.001$). Mean Exo1 almost doubled Exo2, whereas the Exo2 was four-times higher than Exo3 for unburned soils.

Regarding the impact of fire, the total weight loss from 30 to 700 °C (TWL) was considerably less in the burned soils in comparison to the unburned areas (Table 2). The weight loss from 200 to 700 °C (WL) was also lower at the burned plots, indicating a lower amount of organic compounds after the fire. The highest decreases of this parameter were found at sites B1, B2 and B3. The TG results demonstrated that organic compounds were in general more recalcitrant in burned soils (Figure 4). For unburned soils, the relative weight loss for the labile pool (Exo1) was on average 60% of the WL, whereas recalcitrant (Exo2) and refractory (Exo3) ones reached 32.3 and 7.8% respectively. Burned sites showed an average decrease of 7.9% in the labile pool, and an increase of 3.5% and 4.4% in recalcitrant and refractory pools respectively. As also found in the evaluation of thermal stability and weight loss, zones B1 and B3 and, to a

lesser extent B2, showed the more notable changes in organic pools distribution (variation in Exo1 ranging from 7 to 16%).

Despite the substantial variability in TOC amount observed between the unburned soils (coefficient of variation -CV- reaching 39.7%), the SOM composition represented by the distribution of the different organic pools showed a more homogenous trend. On average, the CV of the labile pool was 3.5%, 6.5% for the recalcitrant pool and 7.7% for the refractory pool in all unburned soils. SOM composition at the burned sites, however, showed a considerably higher variability (CV was 16.0, 18.7 and 17.2% for labile, recalcitrant and refractory pools respectively), which could be related to differences in soil burn severity and post-fire recovery experienced by the sites.

From the point of view of the thermal stability of the soil organic compounds, it is important to note that temperature peaks increase from unburned to burned samples (Figure 4). Although no major changes were observed in the Exo3 peak temperature (0.3 °C on average), Exo1 temperature increased by 19.9 °C mainly due to the increase in zone B1, B2 and B3; and Exo2 by 12.1 °C due to zone B1, B3 and, to a lesser extent, B4. T_{50} also increased by 16.0 °C from unburned to burned soils mainly due to the higher values reached by sites B1, B2 and B3 in relation to their controls (Table 2).

3.3 TG as a predictor of post-fire runoff- and erosion-related soil properties

Previously measured soil properties relevant to runoff and erosion were linked to the different indexes accounting for SOM content and composition produced for this study: (i) TOC and the general TG thermo-oxidative step parameters (Endo0, Exo1, 2 and 3), and (ii) the novel indexes associated to the weight losses for each 10 °C temperature

range obtained by TG. The TOC and SOM pools at the four different thermo-oxidative steps (Endo0, Exo1, 2 and 3) showed a lack of correlation for some parameters (clay content, BD, WP and SC), moderate correlation coefficient for FC (explaining up to 70% of the sample variability), moderate-low association for logWDPT (explaining more than 55% of the sample variability) and low for AS and RR (explaining less than 40% of the sample variability) (Table 3).

The correlation of the weight losses for each 10 °C temperature interval with the soil properties evaluated (Figure 5) showed that weight losses related to the Endo0 presented a noticeably positive influence mainly on properties related to porosity such as BD (mainly weight loss in the range 60-100 °C) and WP (60-90 °C) and it was secondary and positively involved in AS (80-120 °C), and negatively in FC (80-100 °C). Weight loss at the Endo1 range was the main factor affecting positively AS (220-330 °C) and WDPT (250-350 °C), whereas, to a lesser extent, it also influenced positively BD (from 260-310 °C) and negatively FC (240-320 °C). At Exo3 range weight loss correlated positively mainly with and FC (440-560 °C and 630-650 °C) and negatively with AS (520-560 °C and 620-640 °C) and BD (560-620 °C). Besides, Exo3 correlated negatively with WP (640-650 °C), although to a lesser extent. Clay content correlated with weight loss in the boundary of Exo2 and Exo3, at 450-490 °C. Regarding the runoff-erosion processes (Figure 6), weight loss for Endo0 range (60-130 °C) and mainly Endo1 (200-310 °C) influenced negatively SC but it had no major influence on RR. The weight loss at the lower boundary of Exo2 showed its positive influence on RR (370-440 °C), whereas Exo3 did on SC (610-650 °C).

Simple linear regressions were performed between the soil parameters and the result of the addition of the weight losses at 10 °C temperature intervals which had exhibited significant correlations (Figures 5 and 6). As shown in Figure 7, soil properties associated with porosity as BD, FC and WP were closely associated to the TG values, which explained over 70% of the total sample variability. Properties such as AS and WDPT presented moderate correlations explaining almost 60% of the sample variability, whilst clay content had the lowest correlation value ($R^2 = 0.51$). Regarding runoff and erosion processes (Figure 8), the linear regression developed fitted well with SC (explaining over 70% of the variability), but poorly with RR (44%).

4. Discussion

4.1 Pre- and post-fire soil organic matter characteristics

The TG and DTA thermograms obtained for both unburned and burned soils showed the characteristic shape found in previous studies, reflecting distinctive endo- and exothermic reactions which take place at different temperature ranges (Figure 2) (see e.g. De la Rosa et al., 2008a; Duguay and Rovira, 2010; Plante et al., 2009). The results indicate that for the studied soils the mineral fraction apparently had a limited impact on the weight loss (Figure 3) despite the high reactivity of the mineral fraction of Andisols (Van Ranst et al., 2004). The high SOM content of the studied soils could explain this result. Therefore, TG weight loss can be mainly attributable to the SOM with the thermograms showing the following patterns: (i) an endothermic moisture loss between 50 and 200 °C, and the three exothermic decomposition reactions range from (ii) 200 to 380 °C for aliphatic C and carbohydrates such as cellulose (labile pool), (iii) 380 to 475 °C for the aromatic-rich constituents as lignin (recalcitrant pool) and (iv) 475 to 700 °C for the polycondensed aromatic carbon such as black carbon (refractory pool).

In general, the results showed high values of ExoTot, highlighting the abundance of SOM in these soils in their undisturbed condition (Table 2) as reported previously (see e.g. Hoyos and Comerford, 2005; Neris et al., 2012). The high weight loss from the Endo0 for unburned Andisols and the relation of this value with the water content of the air-dried samples highlights the increased microporosity traditionally attributed to the undisturbed Andisols in comparison to other soil types (Buytaert et al., 2002). In addition, the SOM composition represented by the three different exothermic steps highlights the importance of the labile pool and the low content of refractory compounds in the undisturbed Andisols (Figure 4) in comparison to other soil types studied using the same methodology (see e.g. De la Rosa et al., 2008a; De la Rosa et al., 2008b).

The relative homogeneity observed in the SOM composition between the different unburned soils is important in terms of using this parameter to evaluate the soil burn severity (Figure 4). It has been stated that most soil burn severity metrics based on organic matter consumption and critical soil properties show noticeable subjectivity and relativity when they compare pre- and post-fire conditions (Keane et al., 2012). As highlighted by these authors, representative unburned areas are not always available due to the wide range of ecosystems usually affected by a fire (represented in this study by the substantial within and between site heterogeneity on SOM amount and critical properties of soils sharing the same classification at order/suborder level and vegetation type). Although further studies involving other ecosystems and soil types are needed, the substantial higher homogeneity of the soil organic matter composition found here, in comparison to its content and other soil properties evaluated, suggests that SOM

composition can serve as a simple proxy for soil burn severity using a limited number of control areas.

Regarding the medium-term impact of fire on soil organic compounds (Table 2 and Figure 4), the results obtained using TG agreed with those widely reported by other authors with respect to the negative impact of fire on the organic matter (see e.g. Certini, 2005; González-Pérez et al., 2004). The decrease in the amount, and the change in the biochemical composition of the SOM as a consequence of both the fire and the partial vegetation and soil recovery have been reported previously (De la Rosa et al., 2008a; Rovira et al., 2012; Salgado et al., 1995). Medium-term fire impacts are generally represented by an increase in the thermal stability of all SOM pools and a change in the SOM composition from the labile to the recalcitrant and ultimately refractory pools due to polycondensation processes that produce more stable organic compounds during burning (De la Rosa et al., 2008a). The TG results obtained here therefore suggest that the medium-term impact of the fire on SOM might be classified as moderate-high for site 1 and moderate for sites 2 and 3 according to the substantial differences between burned and unburned zones in ExoTot, T₅₀, peak temperatures and Exo1, 2, and 3 values. At sites 4 and 5, fire impacts on SOM may be classified as light or absent because no major changes in composition of the SOM were found between burned and control zones.

4.2 Link between TG results and soil physical/hydrological properties

It is widely accepted that the impact of fire on soil physical properties mainly occurs through its influence on the SOM content and composition (Keeley, 2009). A large number of studies have focussed on evaluating soil physical properties after fire such as

soil structure (see e.g. Giovannini and Lucchesi, 1983; Mataix-Solera et al., 2011), soil water repellency (see e.g. Atanassova and Doerr, 2011; Martínez Zavala et al., 2009) or water storage (see e.g. Boix-Fayos, 1997; Stoof et al., 2010). Most of them have pointed out the quantity and composition of the SOM as a key to the behaviour of these properties. Bearing in mind this critical link, most of the correlations between TG analysis and soil physical properties obtained in this study were not unexpected (Table 3 and Figures 5 and 6).

Tisdall and Oades (1982) previously reported that labile forms of C have a major influence on the amount and stability of macroaggregates (>0.25 mm). This is supported by our results by the correlation between the structural stability and the labile (positive) and refractory (negative) SOM. However, here the decrease of the labile pool (Exo1) and, thus, AS as the burn severity increases has led to a decrease of BD. Most authors have reported an increase in bulk density after fire for different soil types (see e.g. Giovannini and Lucchesi, 1997; Hubbert et al., 2006). In contrast, studies performed in Andisols have shown that the drying processes and the decay in organic matter content caused by agricultural use lead to a loss of soil cohesiveness and result in low-density aggregates that are easily eroded (Hernández-Moreno et al., 2007). Potential similarities between the medium-term impacts of fire examined here and those reported following agricultural use regarding to the loss of organic matter and the exposure of the soil to frequent wetting-drying processes may be the reason for this particular behaviour in Andisols. Also, the rise in Exo3 after the fire indicates an increase in black carbon-like material into the soil profile (De la Rosa et al., 2008b). The low bulk density of these charred organic components (see e.g. Bodí et al., 2014; Cerdà and Doerr, 2008) could have reduced BD, as depicted by its positive relation with Exo3.

Water retention capacity was affected by the impact of burn severity on SOM and BD depending on the pF considered. The studies available show that the SOM composition plays a major and complex role for this property. Naeth et al. (1991) published different values of water retention at field capacity for litter samples according to their size and degree of decomposition, whereas Rawls et al. (2003) suggested that water retention capacity was linked to SOM quantity and composition through their influence on the soil structure and adsorption properties. Stoof et al. (2010) found that water retention capacity of burned soils varied differently at different pressures according to the heating temperature, degree of combustion and amount of ashes incorporated into the soil; parameters which are directly connected to both SOM quantity and composition. The positive and negative relation of FC and WP respectively with Exo3, the range usually assigned to the black carbon-like material (De la Rosa et al., 2008b), agrees with the result obtained by Stoof et al. (2010) regarding the positive impact of these compounds on water retention at low tensions. The positive relation between WP and Endo0 could be attributable to the influence of the microporosity on water retention at high tensions, as weight loss at this temperature range was observed to correlate directly with the water content of the air-dried samples. Regarding the clay content, it showed a correlation with the weight losses at the temperature range where the thermal decomposition of 1:1 clay minerals (such halloysite for volcanic soils) occurs. With respect to water repellency, its positive correlation with the labile SOM pool and, complementary, its negative one with the refractory pool (Exo3) may be related to the alteration of the organic matter components due to increased temperatures. Some authors have reported that soil water repellency decreases as heating temperature

increases due to the destruction of the labile organic forms inducing this property (Dlapa et al., 2008).

Regarding the hydrological parameters, although a positive correlation between TC and RR was found, most studies have reported the opposite trend as SOM has a positive influence on soil structure and thus infiltration capacity (Lado et al., 2004; Le Bissonnais and Arrouays, 1997). However, it is also the case that an increase of the total or part of the SOM pool can enhance soil water repellency and, thus, runoff (Doerr et al., 2000). TOC did not show any correlation with WDPT, although it did correlate with Exo1+Exo2 (data not shown in Table 4; Pearson-r: 0.914; $p < 0.001$), which in turn are directly correlated with soil water repellency through Exo3. Thus, the relationship between the SOM content and RR may be explained via the correlation of TOC with SOM composition and water repellency. The lower limit of the temperature range correlated to RR (380 °C) was close to the upper limit of the one correlated to WDPT (350 °C), reinforcing the positive relation between these two properties. It is also worth considering here that subcritical soil water repellency has been found to be a common feature of many soils reducing infiltration and increasing runoff, even when they are classified as not water repellent when using the WDPT test (Hallett et al., 2001). As these authors stated, subcritical water repellency is closely linked to the organic compounds forming hydrophobic coatings on aggregates. Thus, although not examined here, the presence of subcritical water repellency may explain the positive link between TOC and RR, and also the absence of relationship between TOC and WDPT. Finally, the negative correlation of SC with Exo1 and positive with Exo3 may be supported by the effect of fire on soil properties relevant to erosion. The decrease of the labile and increase of the refractory pool reflect a more severe impact of fire on soil properties

such as structural stability or even BD (correlation with Exo1) and, thus, it strengthens the erosion of detached and low-density soil particles.

Overall, none of the thermo-oxidative steps on their own proved to be effective in predicting accurately the medium-term impacts of fire on the whole set of soil properties and parameters related to the runoff and erosion processes examined here (Table 4). However, simple linear regression using the sum of selected weight losses in 10 °C intervals, which correlated with the soil parameters (Figures 5 and 6), allowed predicting the post-fire trends in all of the hydrological properties included in this investigation with a moderate to high level of confidence except for clay content and RR (Table 5 and Figures 7 and 8). Regarding the former, a robust association with the TG data, similar to that found by Siewert (2004), was expected. However, the apparent limited influence of the mineral fraction on the TG results of the evaluated soils stated previously, along with the widely known problems in quantifying clay content in volcanic soils due to incomplete clay dispersion (Armas-Espinel et al., 2003; Bartoli et al., 1991) may have affected negatively the association between both parameters. With respect to the runoff, although SC data reported by Neris et al. (2013a) showed a unique pattern in the medium-term after the fire, it did not regarding RR. The authors assumed that the wide range of soil properties affecting this process, including the forest floor characteristics (Neris et al., 2013b), and the varied impact of the fire on them could explain the inconsistent behaviour of RR among the study sites. This may well have also been the reason for the low R^2 obtained here.

4.3 Usefulness and implications of TG method to predict soil properties

Predicting the impact of fire on the immediate and medium-term runoff and erosion processes is one of the main challenges for land managers and researchers involved in post-fire assessments so that excessive erosion and flooding can be mitigated. Despite substantial advances over the last decades, the link between soil burn severity metrics and soil properties related to runoff-erosion processes in order to predict rapidly post-fire hydrological processes has remained weak (Moody et al., 2013). The present study has demonstrated the potential of TG analysis for the Andisols terrain examined here to both characterise soil burn severity through the assessment of the fire impacts on soil organic compounds, and to be used as a predictor of fire impacts on soil hydrological behaviour. Although prior to the post-fire sample evaluation a single calibration step is needed to link TG data to the site-specific post-fire soil properties determined by conventional soil analysis methods (using either new or already existing datasets), this methodology avoids carrying out numerous different analyses for hydrology-related soil properties after every wildfire and provides immediate information to evaluate the potential hydrological response of the study area in a rapid single step process after calibration.

From the results, the usefulness of this insight TG analysis could be applied at three levels of ecosystem response evaluation after fire: (i) underpinning other metrics to assess or test soil burn severity through the impact on SOM, (ii) providing rapid and inexpensive proxy for data on fire-induced changes in soil hydrological properties for runoff-erosion models, and (iii) evaluating rapidly runoff-erosion related parameters to assist in predicting the potential magnitude of runoff and erosion events in the post-fire period. Given these potential benefits, further research is warranted to test the validity of this methodology for different soils, fire conditions and post-fire temporal windows.

5. Conclusions

This study evaluates the impact of fire on organic matter composition using TG as well as its influence on key soil physical properties in order to test the ability of TG data to be used as a predictor of post-fire soil hydrological behaviour. The results showed a general decrease in the content of total organic matter and in the relative amount of the labile pool, and an increase in the recalcitrant and refractory pools in the medium-term following fire. The significantly higher homogeneity observed for the organic matter composition in comparison to its content before the fire, may facilitate post-fire assessment by reducing the number of control areas needed and, thus avoiding subjectivity and relativity in the evaluation.

Although the conventional thermo-oxidative steps (Endo0, Exo1, 2 and 3) by themselves did not predict accurately the whole set of soil properties evaluated (clay content, bulk density, aggregate stability, water retention, water repellency, runoff-rainfall ratio and sediment concentration), TG data using 10 °C temperature range steps showed good predictions for most of them. The labile pool showed a broad influence on most soil properties evaluated, the refractory pool and the dehydration range affected, as expected, soil water retention capacity. The recalcitrant pool did not exhibit any relationships with the soil parameters investigated except runoff and clay content at the temperature range associated to the decomposition temperature of 1:1 minerals.

The close links established amongst organic matter composition and most of the soil properties examined using TG, as well as its simplicity, allow this method to be

considered as useful tool which may contribute to the ecosystem response evaluation after fire.

Acknowledgements

The authors thank Vicky Arcenegui (Universidad Miguel Hernández), Cristina Santín, Ian Mugford and Sue Alston (Swansea University) for the laboratory assistance and suggestions. We are also grateful to the Colleges of Science and of Engineering (Swansea University) for the wider logistical support.

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Table 1: Pre- and post-fire main physical properties for the unburned (U) and burned (B) sites. Mean and standard deviation (N = 3 per B or U zone) of the total organic carbon (TOC), clay content (Clay), bulk density (BD), water retention at field capacity (FC), wilting point (WP), aggregate stability (AS) and water repellency (logWDPT).

Site		TOC	Clay	BD	FC	WP	AS	logWDPT
		%	%	Mg m ⁻³	%	%	%	log s
1	U	17.4 ± 2.0	20.3 ± 0.9	0.50 ± 0.08	62.3 ± 8.8	32.1 ± 7.2	48.4 ± 13.2	3.6 ± 0.8
	B	9.0 ± 3.5	17.7 ± 2.3	0.55 ± 0.05	76.8 ± 7.8	27.1 ± 10.6	29.0 ± 9.3	0.4 ± 0.3
2	U	9.5 ± 4.7	20.6 ± 3.7	0.52 ± 0.07	54.5 ± 8.9	20.3 ± 8.9	29.4 ± 5.0	2.9 ± 1.3
	B	5.3 ± 0.6	14.4 ± 3.8	0.47 ± 0.07	41.6 ± 9.9	17.7 ± 7.6	25.7 ± 2.2	0.8 ± 0.5
3	U	15.6 ± 6.1	12.8 ± 2.5	0.77 ± 0.06	68.0 ± 5.4	19.1 ± 0.9	30.9 ± 8.9	2.4 ± 1.2
	B	12.2 ± 2.0	8.9 ± 2.8	0.45 ± 0.03	73.6 ± 1.8	26.6 ± 4.6	21.5 ± 7.9	1.4 ± 0.3
4	U	7.2 ± 2.5	15.0 ± 0.4	0.85 ± 0.02	74.7 ± 11.7	17.3 ± 2.4	44.5 ± 5.5	1.4 ± 0.7
	B	7.2 ± 1.8	14.1 ± 3.5	0.71 ± 0.06	38.0 ± 16.3	17.7 ± 7.1	34.2 ± 5.1	1.8 ± 0.6
5	U	8.3 ± 1.7	20.0 ± 0.2	0.79 ± 0.13	47.4 ± 4.4	28.5 ± 3.8	38.8 ± 5.1	1.6 ± 0.8
	B	6.5 ± 1.4	10.5 ± 0.7	0.49 ± 0.16	46.3 ± 5.4	23.6 ± 6.6	36.0 ± 6.5	2.3 ± 1.5

Table 2: Pre- and post-fire TG parameters in the unburned (U) and burned (B) sites.

Mean and standard deviation of the total weight loss from 30 to 600 °C (TWL), weight loss from 200 to 600 °C (ExoTot), weight loss from 30 to 200 °C (Endo0) and temperature value corresponding to the 50% oxidation of the sample (T_{50}) were calculated.

Site		TWL %	ExoTot %	Endo0 %	T_{50} °C
1	U	41.7±3.6	32.5±3.0	9,18 ± 0,64	360.4 ± 9.3
	B	23.2±6.1	17.2±5.5	6,04 ± 0,93	393.3 ± 11.7
2	U	21.6±8.6	16.8 ± 7.4	4,78 ± 1,28	356.3 ± 7.2
	B	16.3±0.5	11.4±0.8	4,85 ± 0,54	374.1 ± 13.3
3	U	34.4±11.3	27.2±10.7	7,21 ± 0,67	364.1 ± 13.6
	B	24.6±2.9	19.1±2.2	5,46 ± 0,74	394.9 ± 2.1
4	U	18.9±6.1	14.4±5.2	4,48 ± 0,97	351.3 ± 7.3
	B	21.9±4.4	15.6±3.6	6,32 ± 0,82	351.3 ± 5.6
5	U	23.5±2.8	17.2±2.7	6,31 ± 0,03	357.9 ± 1.4
	B	20.8±2.2	14.7±2.4	6,11 ± 0,37	358.1 ± 0.7

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Table 3: Pearson-r correlation coefficients of the main soil properties and parameters related to the post-fire hydrological response.

Clay content (Clay), bulk density (BD), water retention at field capacity (FC) and wilting point (WP), aggregate stability (AS), water repellency (logWDPT), rainfall-runoff ratio (RR) and sediment concentration (SC) as well as the total organic carbon (TOC) and the relative weight loss at the different thermo-oxidative steps (Endo0, Exo1, 2 and 3) (*: P <0.05; **: P <0.01 and ***: P <0.001). Non-significant correlation coefficients were excluded (-: P >0.05).

	TOC	Endo0	Exo1	Exo2	Exo3
Clay	-	-	-	-	-
BD	-	-	-	-	-
AS	-	-	0.616*	-	-0.619*
FC	-	-	-0.832***	0.774**	0.628*
WP ^{1/2}	-	-	-	-	-
logWDPT	-	-	-	-	-0.749**
RR	0.568*	-	-	-	-
SC ^{1/2}	-	-	-	-	-

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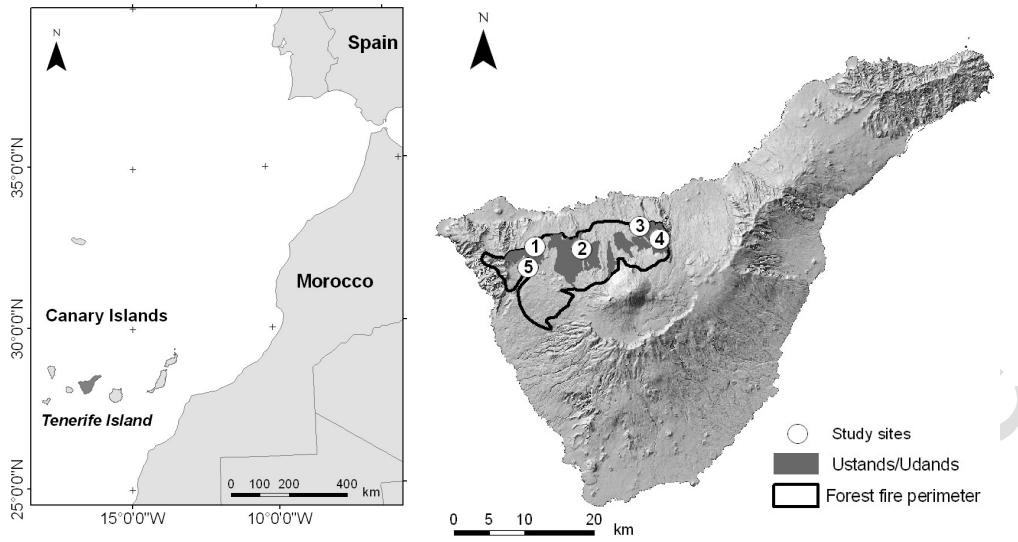


Figure 1: Location of the island of Tenerife, Andisols (Udands and Ustands), burned area and study sites.

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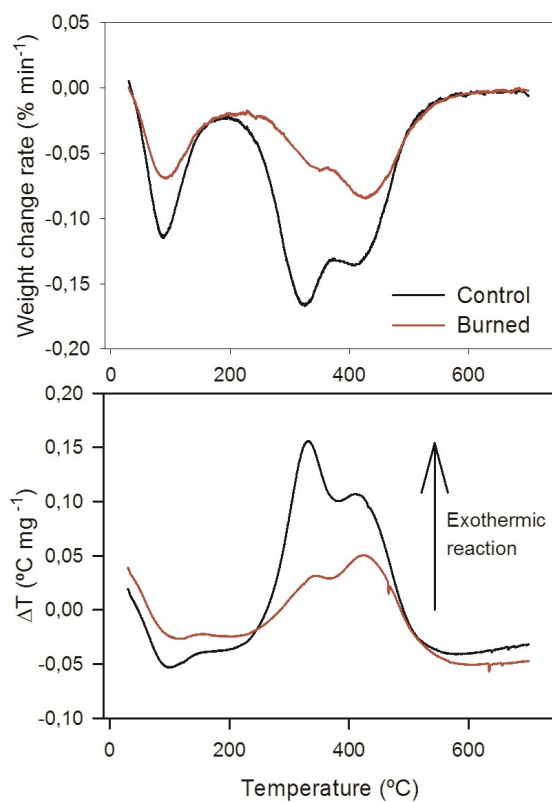


Figure 2: Typical example of thermograms corresponding to DTG (top) and DTA (bottom) of a burned (black) and an unburned (red) study sample (site 1) showing the thermo-oxidative decay steps.

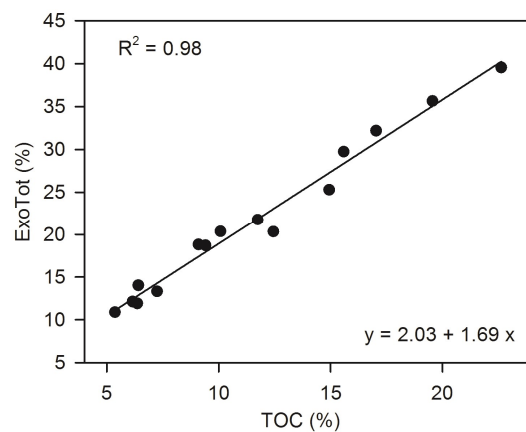


Figure 3: Single linear regression between TOC (x-axis) and ExoTot values (y-axis).

Equation of the line and coefficient of determination (R^2) included.

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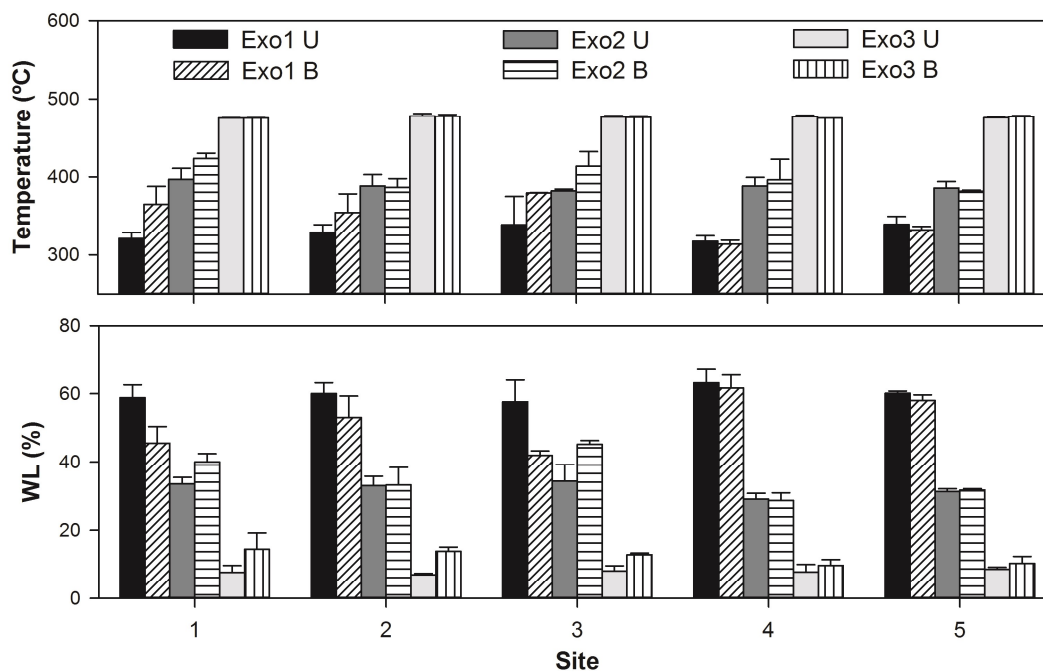


Figure 4: Changes in temperature peak (top) and weight loss (bottom) for each exothermic thermo-oxidative step (Exo1, 2 and 3) for unburned (solid fill) and burned samples (patterned fill) (N = 3 per each B and U sample sites).

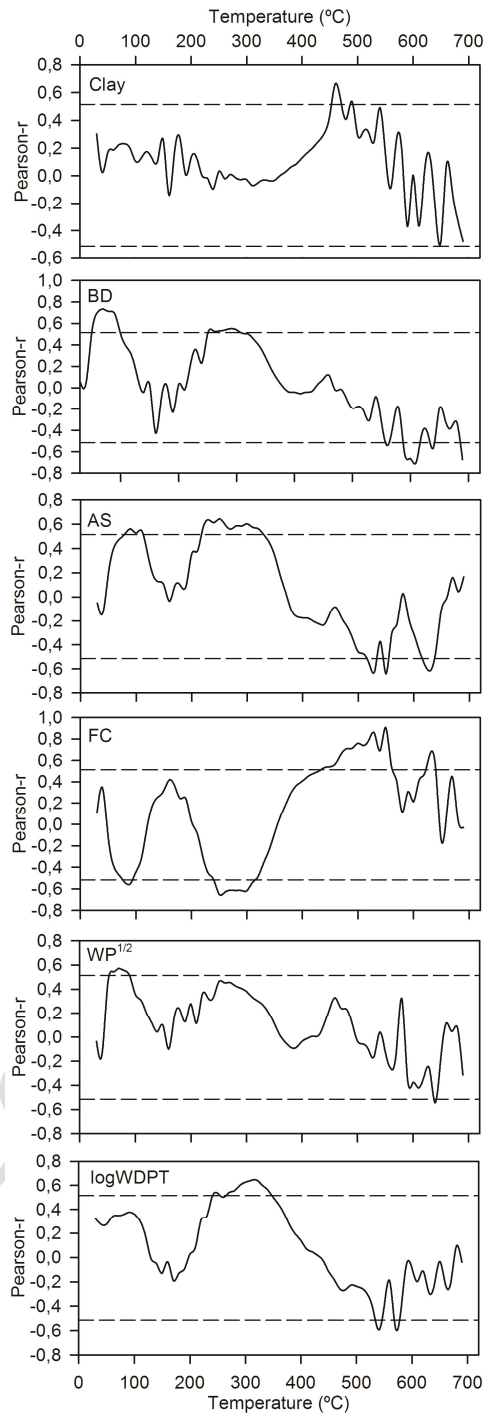


Figure 5: Pearson-r coefficient (y-axis) for the weight losses at different temperature range steps (x-axis) and clay content, bulk density (BD), aggregate stability (AS), field capacity (FC), permanent wilting point (WP) and lognormal water repellency (logWDPT) (y-axis). The horizontal lines represent the significance level for $p < 0.05$.

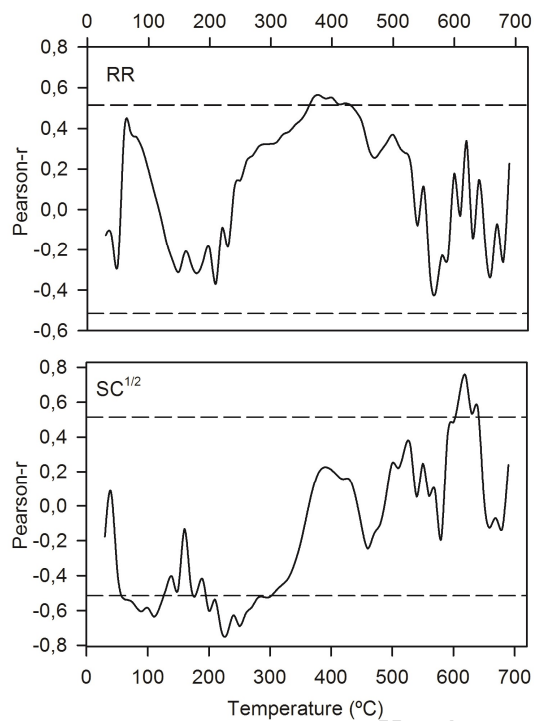


Figure 6: Pearson-r coefficient (y-axis) for the weight losses at different temperature range steps (x-axis), runoff coefficient (RR) and sediment concentration (SC) (y-axis). The horizontal lines represent the significance level for $p < 0.05$.

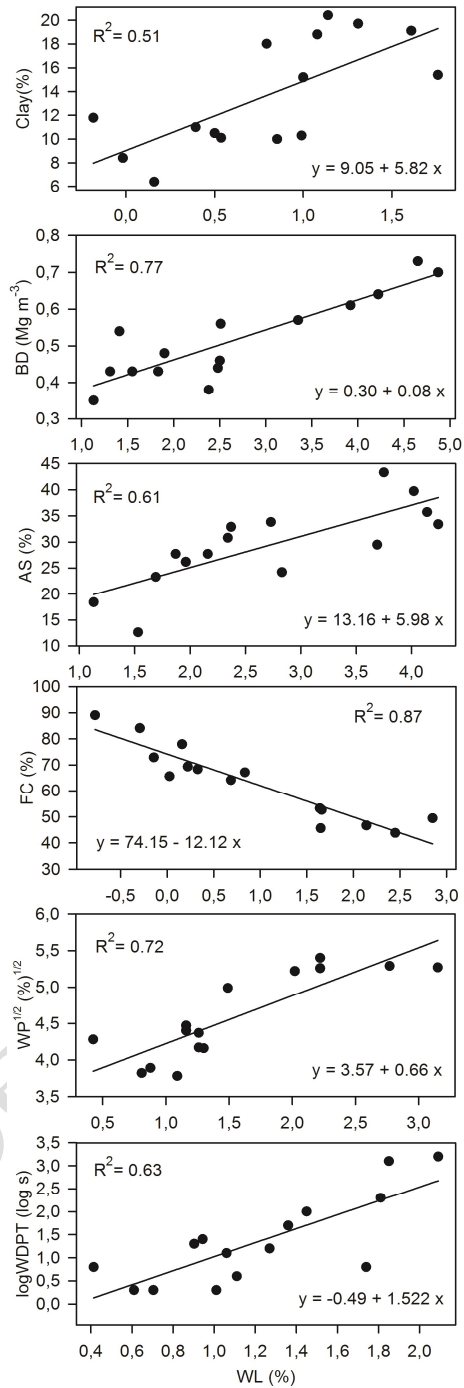


Figure 7: Single linear regressions between weight losses at selected temperature range steps (x-axis) and clay content, bulk density (BD), aggregate stability (AS), field capacity (FC), permanent wilting point (WP) and lognormal water repellency (logWDPT) (y-axis). Equation of the line and coefficient of determination (R^2) included.

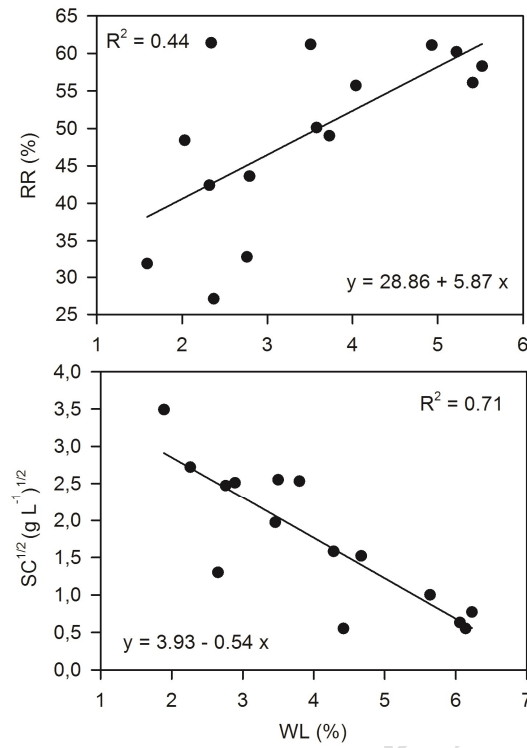


Figure 8: Single linear regressions between weight losses at selected temperature range steps (x-axis), runoff coefficient (RR) and sediment concentration (SC) (y-axis). Equation of the line and coefficient of determination (R^2) included.