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Comparison of two calorimetric methods to determine the loss of organic matter in Galician soils (NW Spain) due to forest wildfires

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Abstract

Seven forest soils, Cambisols under pinus, located at Galicia (NW Spain) and affected by forest wildfires were collected to determine the loss of organic matter due to the effect of burning, using calorimetric methods. The enthalpy of combustion, ΔH, of the organic matter of the burnt and the corresponding unburnt soils was calculated from the thermograms obtained with a differential scanning calorimeter (DSC-7, Perkin-Elmer). From these data, the loss of organic matter during the fires was calculated. On the other hand, the organic matter content for each burnt and unburnt soil studied was determined by thermogravimetry (TG) and, in the same way, the loss of organic matter was obtained. High linear, significant correlations were found between the enthalpy of combustion of the soil organic matter (SOM) and the organic matter content measured by thermogravimetry. Consequently, comparison of the loss of organic matter obtained by both methods indicated that the quantitative results are similar. Both techniques allow to determine the degradation level of the soils affected by forest wildfires, taking the loss of organic matter during the fire as a degradation index.

Keywords: Differential scanning calorimetry; Thermogravimetry; Forest wildfires; Soil organic matter

1. Introduction

The problems and negative impacts of wildfires are increasing worldwide. In the last decades, the number, size and intensity of fires have been growing in several Mediterranean countries, like France, Portugal, Italy, Greece and Spain [1]. More than 6 million hectares, approximately 24% of the total forestal area, have been burned in Spain since 1961. Approximately, 65% of these fires are deliberate and 13% originate by negligence while burning farms to obtain pasture fields [1–4]. Galicia (NW Spain) is one of the most affected regions in this country. This region—considered in the past as an area of relatively low-risk in wildfire because of its climate and the floristic composition of its forests—in the last two centuries was greatly modified by human activities, particularly by the introduction of species more vulnerable to fire [5].

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The effect of the fire is significant on the soil environment in particular, which is directly affected by a supply of ash and heat input, both having a polluting effect [6,7]. Soil heating is also a cause of water repellence in soils potentially leading to erosion, loss of nitrogen, carbon and nutrients and, at extreme levels, to structural changes, with the consequent economic losses and landscape deterioration [1,6–10]. Soil organic matter (SOM) plays an important role in soil ecosystems, mainly due to its cation exchange and water-holding capacities and as a nutrient reservoir [9]. In soils rich in organic matter and low in clay, such as those in Galicia, soil organic matter also controls the available nutrient content for plant growth by the rate of its mineralization process [1]. The fire can remove high amounts of organic matter and it could have negative impacts on site productivity [1,11]. Therefore, calculation of the losses of soil organic matter in soils affected by wildfires is of paramount importance to know soil degradation.

The calorimetric techniques, which are useful tools to analyse some thermodynamical characteristics of the soil, can also be used to determine the effects of the fire on soil organic matter losses, particularly in laboratories where conventional chemical techniques for determination of soil organic matter are not available. Differential scanning calorimetry (DSC) and thermogravimetry (TG) are both physico-chemical techniques, based on computer-controlled heating of the sample in a controlled atmosphere [12]. In the first case, depending on the reactions that occur at the various temperatures, the resulting DSC graph is a curve showing endothermic and exothermic peaks. The positions of the peaks, i.e. the temperatures at which these peaks happen, and the peak areas give information about soil characteristics and organic matter combustion. Thermogravimetry is a technique in which the changes in the soil weight are measured and recorded during the increase in heating of the soil sample [12], the weight losses being directly related with the soil organic matter content.

In a previous work [13], we have described a method to determine the loss of organic matter in soils as a consequence of forest wildfires using a differential scanning calorimeter. In this paper, a new method to determine the organic matter content of the soils using thermogravimetric analysis is explained; from these analyses the loss of organic matter due to the fire can be calculated. The aim of this work is to apply both methods to several soils and to compare the results obtained.

2. Materials and methods

2.1. Soil sampling and treatment

Seven Humic Cambisols developed over granite under pine stands, located in Galicia (NW Spain) at Caldas (province of Pontevedra), Manzaneda (province of Ourense), Retortas (province of Pontevedra), Cervantes (province of Lugo), Villestro and Roxos (province of A Coruña) were studied. These soils were affected by forest wildfires in September 1990, September 1991, July 1992, February 1995, July 1996 and August 2000, respectively. Most of the unburnt soils were sandy, acidic and with a high content of organic matter in the A horizon, this component determines the physical and biochemical properties of soil [14]. The main clay mineral is kaolinite. All the burnt soils clearly showed morphological signs of the fire from the surface (white ashes in Caldas and Manzaneda soils; black ashes in the other soils) down to 5 cm (black ashes in Caldas and Manzaneda soils) with an irregular burning boundary at this depth. Villestro soil showed different signs of the burning at the top (Villestro I) and at the bottom (Villestro II) of the hill and it was sampled in both places. Samples from the surface (0–5 cm for Caldas and Manzaneda soils and 0–2 cm for the rest) and the subsurface (5–10 cm for Caldas and Manzaneda soils) layers of the A horizon of the burnt and the corresponding unburnt soils were collected within the first month after the fire. This was done after removal of the litter layers, which consisted mainly of undecomposed leaves. Sample collection, preparation and chemical analyses of Caldas, Manzaneda and Retortas soils were made by Carballas et al. [14]. The samples from Villestro I, Villestro II, Cervantes and Roxos soils were collected and prepared by Salgado et al. [15,16]. For analysis, visible plant particles were removed from the soil by hand and the samples were sieved at 4 mm. The fraction less than 4 mm was homogenised and used for this study.

2.2. Determination of the enthalpy of combustion of the organic matter

Thermograms of the burnt and unburnt soil samples were carried out using a differential scanning calorimeter (DSC-7, Perkin-Elmer) [12]. These thermograms were obtained under dry air flowing at 2.1 kg cm^{-2} and a scanning rate of 10 °C min^{-1}, using samples between 10 and 30 mg of soil, and pierced aluminium crucibles of 50 μl capacity. The range of temperature was 50–600 °C. Samples of Indium (mp: 156.6 °C) and Zinc (mp: 419.47 °C) were used to calibrate the calorimeter. A total of six replicates per sample were analysed.

The enthalpy of combustion, ΔH, of the soil organic matter was calculated directly from the thermograms, as the area between the baseline of the apparatus and the exothermic combustion peak [12]. This method was widely covered in a previous paper [13].

2.3. Determination of the organic matter content of the soil

The organic matter content for every soil sample was determined using the thermogravimetric analyser (TGA-7, Perkin-Elmer). As explained above, this apparatus measures weight changes in a soil sample as a function of temperature or time; from the loss of weight, the soil organic matter content can be calculated. A thermogravimetric analyser [12] working under flowing dry air, with a scanning rate of 10 °C min^{-1}, was used. The soil samples were about 30 mg in weight. The range of temperature was 50–800 °C. Samples of nicoseal and perkalloy, which present the magnetic transition temperature at 438 and 596 °C, respectively, were used to perform the temperature calibration, and a 100 mg calibration standard weight was used to perform the weight calibration [12]. A total of six replicates per sample was analysed. Fig. 1a shows the thermogravimetric curve of a soil sample, where the weight loss of the soil sample due to the heating effect against temperature can be seen; a high weight loss appears approximately between 200 and 600 °C, which agree with the temperature range previously determined by DSC for combustion of the soil organic matter (Fig. 1b) [13]. Therefore, the loss of weight produced in the sample between the above-mentioned temperatures, after an experience in the TGA-7, is equal to the

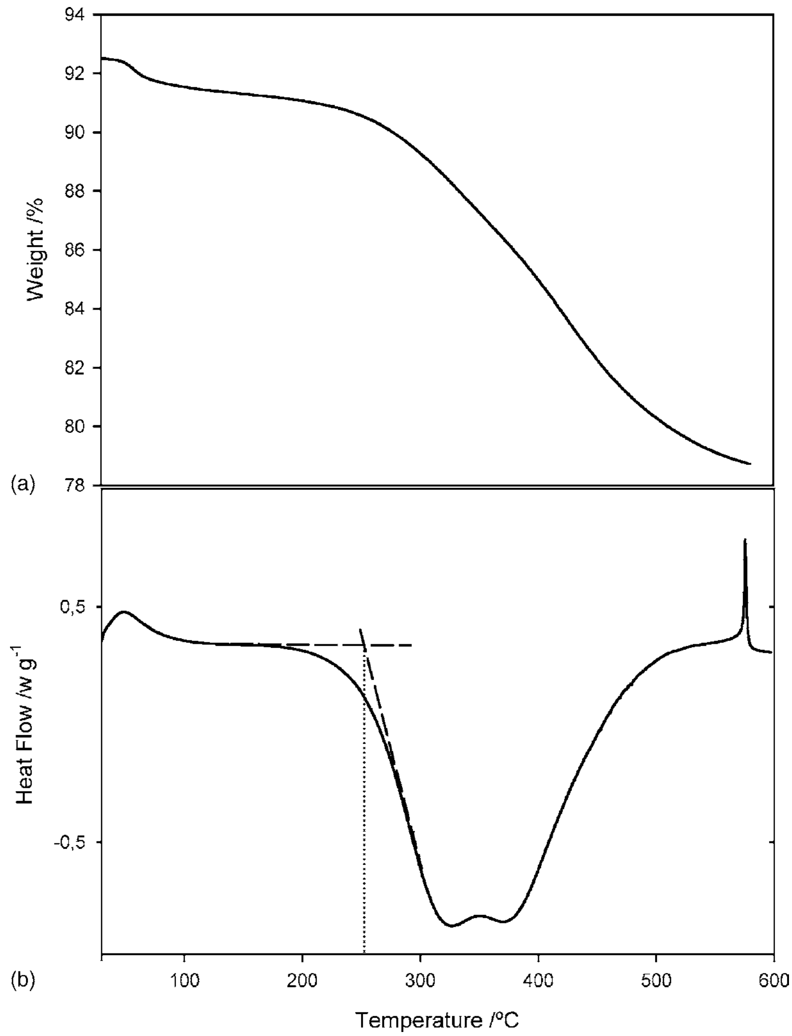

Fig. 1. (a) Thermogravimetric curve of a soil sample and (b) thermogram of the same soil sample obtained by differential scanning calorimetry.

organic matter content (%) in the soil sample before the heating.

2.4. Calculation of the loss of soil organic matter due to forest fires

From the two methods described above, the loss of organic matter of the soils affected by forest fires could be calculated. Using the DSC, the enthalpy of combustion of the burnt, ΔH_b, and the corresponding unburnt soils, ΔH_u, were determined. Taking into account that, for each soil, the energy liberated is proportional to the amount of organic matter destroyed during the combustion, the loss of organic matter of the soils (L) was calculated by the expression $L(\%) = 100(\Delta H_u - \Delta H_b)\Delta H_u^{-1}$ [13]. By thermogravimetric analyses, the organic matter contents for the unburnt and the corresponding burnt soils were determined. For each soil the difference between both contents gave the organic matter lost during the wildfire.

3. Results and discussion

3.1. From differential scanning calorimetry

All the thermograms obtained (Figs. 2–5) presented three peaks. The first peak, which is endothermic, appears between 50 and 150 °C and is attributed to dehydration and loss of volatile substances; the second peak, which is exothermic, appears between 200 and 575 °C and, as shown in a previous paper [13], is due to the combustion and degradation of the soil organic matter. This peak can be considered as the overlapping of two exothermic peaks corresponding to two fractions having different thermal stabilities [13,17,18]. Similar exothermic effects have been reported using DTA/DSC for other soils, lignites and coals [19–21]. The last peak, which appears at approximately 575 °C, is endothermic and seems to be of inorganic origin [13,22]. Taking into account that the soils were over granite and that the sandy fraction was mainly composed of quartz, the peak was attributed to

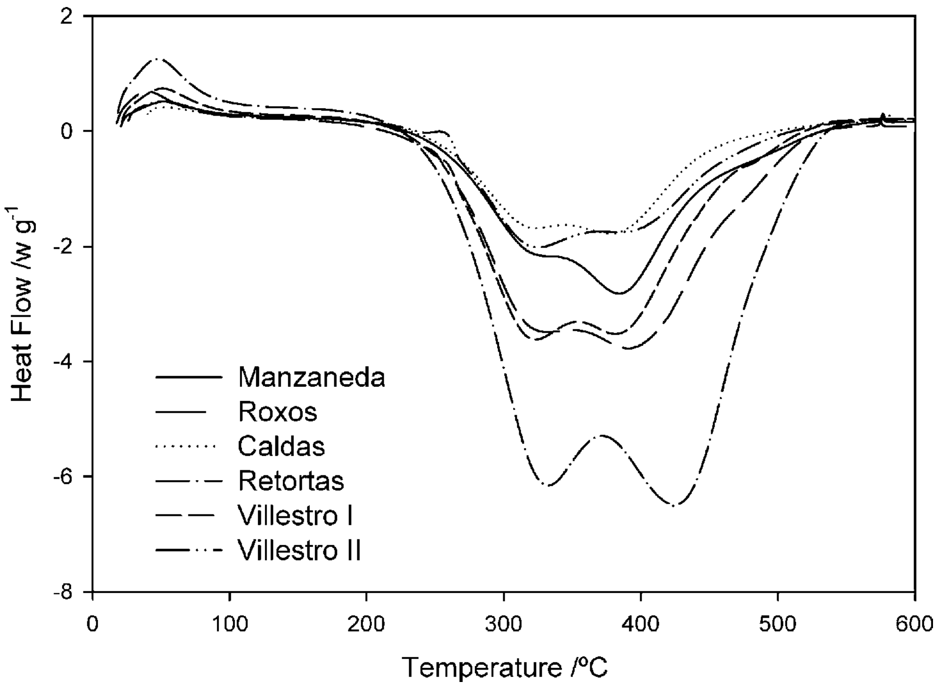

Fig. 2. Comparison among the thermograms of the different unburnt soils.

the polymorphic transformation of hypothermic quartz to hyperthermic quartz, which starts at that temperature [22].

The thermograms of the unburnt soils (Fig. 2) presented different characteristics, which concern the shape of the peaks, the temperature at which the minimum appears and the values for the enthalpy of combustion. Thermograms of the Retortas, Manzaneda, Caldas and Cervantes soils showed the second of the two overlapping peaks larger than the first, that of the Roxos soil presented both peaks with similar area and those of Villestro I and II exhibited the first peak as the largest one. These exothermic peaks were more separated in Retortas and Roxos soils; in these soils the second minimum appeared at temperatures higher than 400 °C, whereas the rest of the soils presented it at temperatures lower than

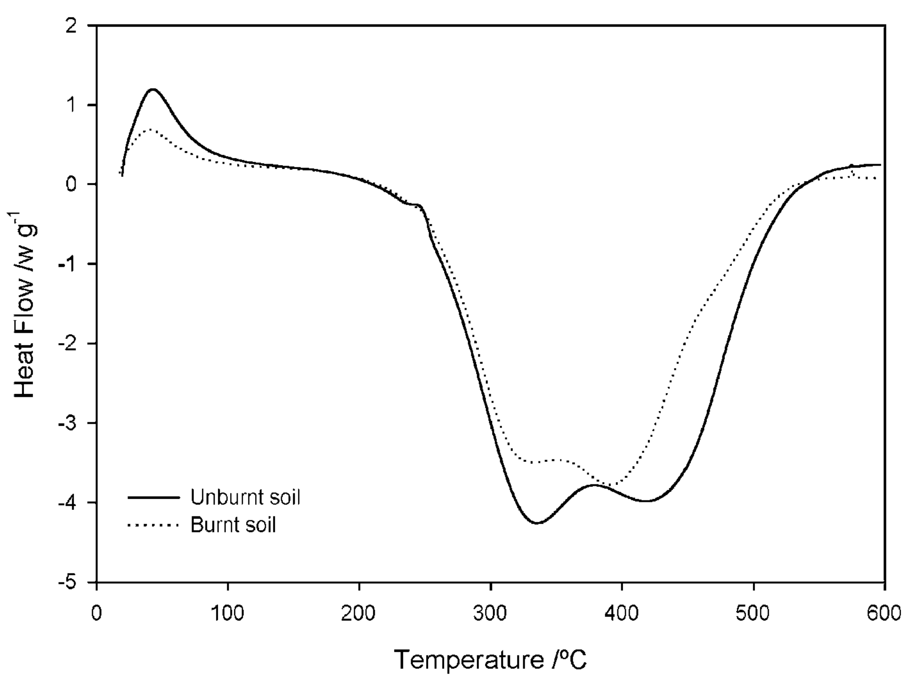

Fig. 3. Thermograms of the Roxos burnt soil and the corresponding Roxos unburnt soil.

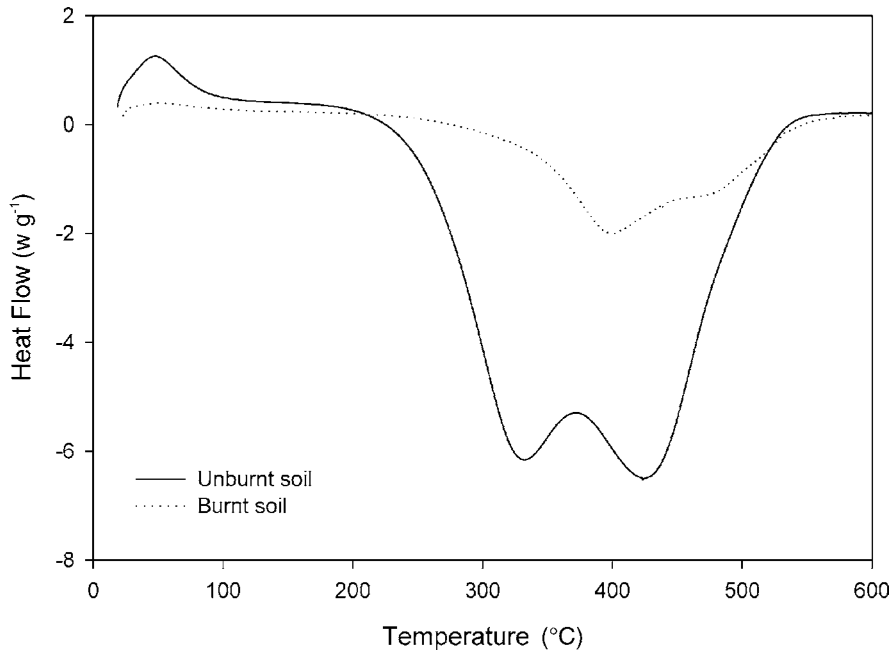

Fig. 4. Thermograms of the Retortas burnt soil and the corresponding Retortas unburnt soil.

400 °C. The highest value for the enthalpy of combustion corresponded to the Retortas soil, and the lowest values were exhibited by the surface layer of the Caldas soil and the subsurface layer of the Manzaneda soil (Table 1). These facts are indicative of the heterogeneous nature of the organic matter and its stepwise combustion rather than a continuous process [21] and of the different characteristics of the organic matter of the soils studied.

Figs. 3 and 4 show that the thermograms of the burnt and the unburnt soils presented the most important differences in the second peak. This exothermic peak decreased in all the burnt soils sampled, and the two overlapping peaks merged into a single one in almost all the burnt-soil thermograms, being specially dramatic in the Retortas soil, where it was almost lost (Fig. 4). Gibbs et al. [21] found only one exothermic peak in soil samples with low organic

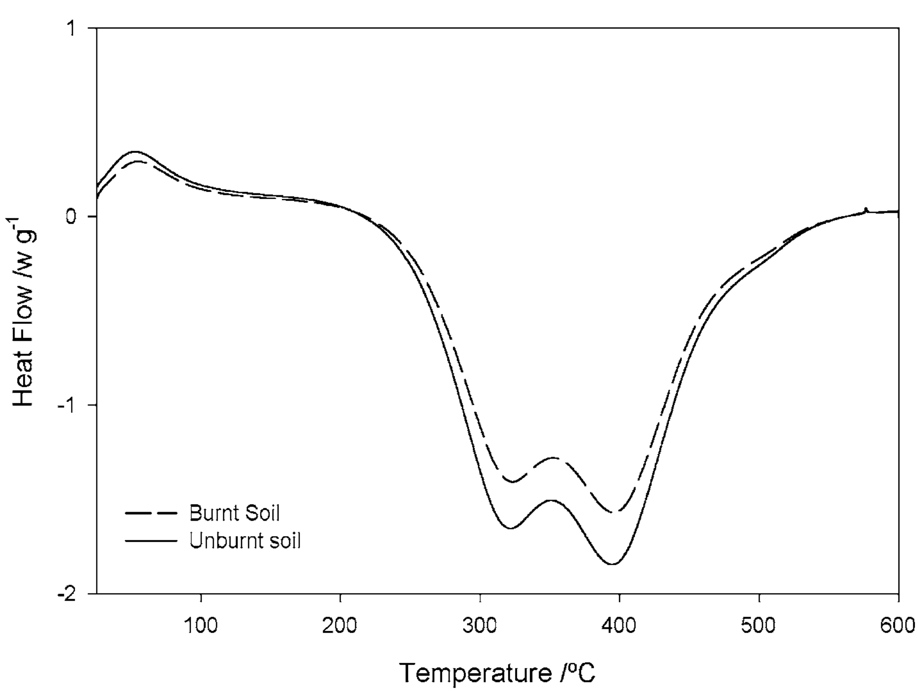

Fig. 5. Comparison between the thermograms of the unburnt and burnt Cervantes soils.

Table 1
Mean values ± confidence interval ($P < 0.05$, $n = 6$) of the enthalpy of combustion ($kJ\,g^{-1}$) of the soil organic matter (SOM) for the unburnt and burnt soils and loss of the SOM (%) due to fires, calculated from the enthalpy of combustion

Soil	Unburnt	Burnt	SOM loss (%)
Manzaneda (0–5 cm)	−3.0 ± 0.8	−1.6 ± 0.8	47
Manzaneda (5–10 cm)	−2.3 ± 0.5	−1.5 ± 0.3	35
Caldas (0–5 cm)	−2.3 ± 1.0	−1.8 ± 0.5	22
Caldas (0–5 cm)	−3.1 ± 1.0	−1.9 ± 0.5	39
Retortas	−8.7 ± 0.5	−3.0 ± 0.5	66
Villestro I	−6.5 ± 2.3	−4.9 ± 1.0	27
Villestro II	−5.1 ± 1.3	−2.8 ± 1.3	45
Cervantes	−2.7 ± 1.0	−2.5 ± 0.8	7
Roxos	5.5 ± 0.8	4.6 ± 0.3	16

matter content, which agrees with our results for burnt soils.

The mean values of the enthalpy of combustion of the organic matter for all the soils are shown in Table 1. It can be observed that the burnt soils had lower values than unburnt soils, except the Cervantes soil, where the enthalpy of combustion of the burnt soil was similar to that of the corresponding unburnt soil. These results can be explained taking into account that part of the soil organic matter disappeared as an effect of the forest wildfire, as it could be expected, and that in the Cervantes soil (see Fig. 5), which got burnt in winter, the fire impact was lower than in the rest of the soils, burnt in summer.

The losses of soil organic matter calculated from the enthalpy of the organic matter of the burnt and the unburnt soils are also shown in Table 1. In general, organic matter losses exhibited high values, particularly the Retortas soil, which indicate that the soils were affected most by fires with high intensity and soil degradation was high as well. Therefore, it is likely that they will need several years to recover the initial properties [19]. On the contrary, the Cervantes soil, which was affected by a winter fire—when the weather and vegetation are probably not suitable for the soil to reach high temperatures—the organic matter was not affected considerably. Data also show the difference in the effect the fire had on the top and the bottom of the hill, with a higher loss of the soil organic matter at the bottom where an accumulation of organic matter is more likely. These results agreed with the results obtained by Carballas et al. [14], Fernández et al. [5], Prieto-Fernández et al. [23], Fernández et al. [24], and Fernández et al. [25], who studied the changes triggered by fire on soil organic matter.

3.2. From thermogravimetry

Fig. 6 shows the thermogravimetric curves of the burnt and the unburnt Retortas soils. It can be observed that the weight loss was much higher in the unburnt soil than in the burnt soil, which is in agreement with the enthalpy of combustion results obtained with DSC explained previously.

The mean values for the organic matter content of the soils are shown in Table 2. The loss of organic matter due to fire, calculated from data of the organic matter content in the burnt and the corresponding unburnt soils, is also shown in Table 2. It was not possible to calculate the loss of organic matter on the Cervantes soil because the content of organic matter was similar in the burnt and the corresponding unburnt soil.

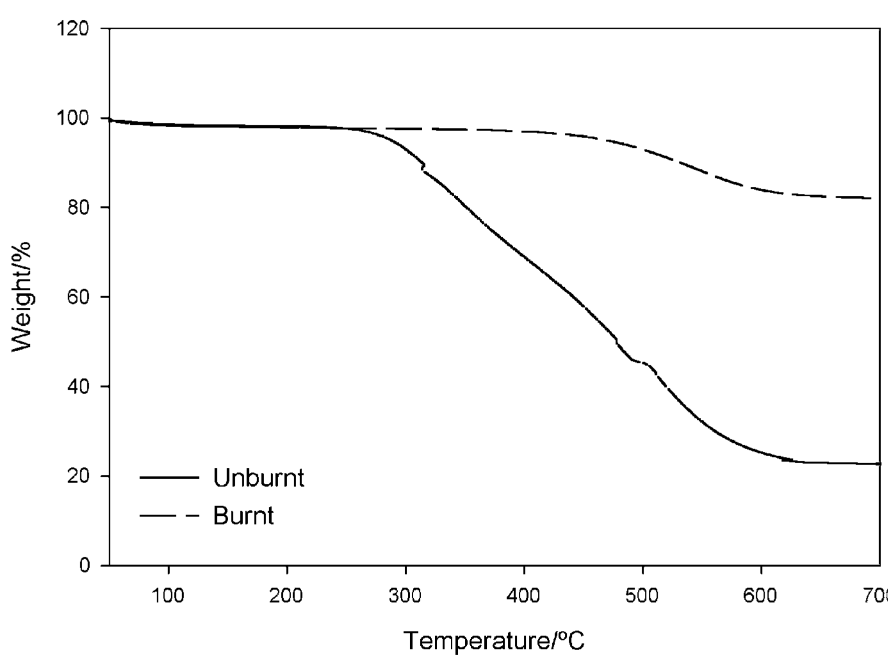

Fig. 6. Thermogravimetric curves of the burnt and unburnt Retortas soils.

Table 2
Mean values ± confidence interval ($P < 0.05$, $n = 6$) of the soil organic matter (SOM) content (%) for the unburnt and burnt soils, and loss of SOM (%) during the fires, calculated by thermogravimetry

Soil	Unburnt	Burnt	SOM loss (%)
Manzaneda (0–5 cm)	27.0 ± 1.0	12.6 ± 1.0	53
Manzaneda (5–10 cm)	19.2 ± 1.6	10.7 ± 0.8	44
Caldas (0–5 cm)	17.8 ± 0.8	15.4 ± 0.8	13
Caldas (5–10 cm)	23.4 ± 3.6	17.3 ± 0.8	26
Retortas	65.3 ± 4.0	20.2 ± 5.9	69
Villestro I	52.0 ± 3.3	40.4 ± 1.8	22
Villestro II	29.0 ± 0.2	14.9 ± 1.5	48
Cervantes	25.7 ± 0.8	25.7 ± 1.3	–
Roxos	30.7 ± 2.6	25.8 ± 3.3	16

Correlation analysis was used to test the relationship between the enthalpy of combustion of the soil organic matter and the organic matter content of the soil measured by thermogravimetry [26]. As expected, high linear correlations between both parameters were found for the unburnt ($r = 0.96$, $P < 0.001$) and the burnt soils ($r = 0.92$, $P < 0.001$).

Consequently, with these correlations, a comparison between the loss of organic matter obtained by both methods indicated that the results are similar, the only exception being the layers of the Caldas soil, which, on the other hand, present a quite strange behaviour, with higher values in the subsurface layer than in the surface one. This trend was also found by Fernández et al. [24].

4. Conclusions

Two calorimetric methods were used to analyse the effect of forest fires on soil organic matter losses. The heating between 200 and 575 °C caused the combustion of the organic matter of the soil, obtaining the same limits by differential scanning calorimetry and thermogravimetry. By DSC, the enthalpy of combustion of the organic matter was determined in several burnt and the corresponding unburnt soils from Galicia (NW Spain). By TGA, the content of organic matter in all the soils was measured. Using both variables the loss of organic matter was determined. High concordance between results from both methods were found.

The burnt soils showed lower values of the enthalpy of combustion and organic matter content than the corresponding unburnt soils in all the samples studied, the difference being the highest in the Retortas soil in both cases, which shows the highest loss of organic matter during the forest wildfire.

These new techniques allows determining the degradation level of the soils affected by forest wildfires taking the loss of organic matter during the fire as a degradation index.

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