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# Effect of the soil uses on their thermal stability

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**Abstract** Differential scanning calorimetry was applied to assess on seasonally soil organic matter changes. Soils were collected in two sites located in Viveiro (Galicia, Spain). One of them has been used as arable land and the other one was under pinewood. Soil samples were seasonally collected during a year. The heat of combustion and the ignition temperature of the soil organic matter were calculated by analyzing the thermograms obtained by differential scanning calorimetry. The shape and the maximum and end temperatures of the two exothermic peaks observed in the thermograms, yielded information about the relations between the labile and recalcitrant pools, and hence information about carbon stabilization degree in both soils.

**Keywords** DSC · Heat of combustion · Recalcitrance · Soil organic matter · Soil quality

## Introduction

The *Kyoto Protocol*, an international environmental treaty of the United Nations Framework Convention on Climate Change (UNFCCC or FCCC), is intended to achieve the stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Although the burning of fossil fuels has been the major cause of the emissions of the green house gases, the agriculture and land use still contribute about 20% of the anthropogenic emissions [1]. Managed land in agriculture and forestry are important parts of the global carbon cycle, and the management practices used can determine whether these lands are sources or sinks of carbon. In this sense, the Kyoto Protocol demands the understanding of carbon stabilization in soils because their organic matter represents one of the largest reservoirs of organic carbon on global scale.

Besides the environmental benefits, increasing the levels of organic matter can provide agricultural profits like the improvement of soil fertility and the stimulation of biodiversity. The amount of soil organic matter and its components are important indicators of soil quality and health, and this is directly influenced by land management practices [1].

The quality of the soil organic matter is related with its difficulty to be degraded by the microflora [2] and depends on its composition: labile components are degraded first, while the recalcitrant one can remain for many years. There are several parameters to measure the quality of soil organic matter, one being the most classic C/N ratio [3] which is basic for determination of the soil mineralization degree, and gives information about the potentiality to generate macronutrients to support the sustainable productivity of soil and its correct development.

In the last decades, the thermal methods have taken relevancy in soil studies. They have been used to characterize chemical changes in organic matter, to determine the impact of forest fires [4, 5], to assess on the effects of changes in land management practices [6] and changes after reforestation [7], to know the impact on soil of the

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addition of fertilizers [8] and to study composed materials from different sources [9].

In this work, differential scanning calorimetry (DSC) in air atmosphere is used to study the thermal properties of the soil organic matter (SOM) [2, 10, 11]. The main goal is to assess on the sensitivity of those properties to seasonal climatic variations and to check the role of DSC on the stabilization of the SOM in soils under different managements.

## Materials and methods

### Sampling

Samples from two soils located in Viveiro, Galicia, NW Spain, were collected during 1 year at the end of the four seasons (summer, autumn, spring and winter). These soils, a humic-eutrophic Cambisol soil, have a geological substrate consisting of slate and filites, with the same origin and identical physical environmental conditions, but under different agricultural exploitations, one is a corn and bean arable land and the other one is a pine soil reforested 15 years ago.

The main physical characteristics of arable soil are stable–moderate, subangular–angular structure with slight quantities of stones and aggregates with a high degree of stability. The aggregates are bigger than 0.40 cm with an average distribution of 68.8% fine (<0.40 cm) and 31.2% thickness (>0.40 cm). Degree of development pedial moderated with structural thick class.

The pine wood soil has a high presence of organic matter (roots, leaves, bark, etc.) and presented as main physical characteristic a low stability with fine dust and little stones (0.27–1.00 cm). The structure can be classified as subangular–granulate composed with aggregates (>1.00 cm) with an average distribution of its different components of 39.1% fine (0.27–1.00 cm) and 60.9% bulky (>1.00 cm). The slate is the most abundant component.

Sample collection took place in 100 $m^2$ of a land area divided into 1 $m^2$ sites, six of which were randomly chosen after eliminating those situated in the borders [7]. Before collecting samples, the plant litter on each site was removed and then 1 kg of soil was taken from a depth of 5–15 cm. The sample was reduced through a coning and quartering procedure to a final size of about 400 g to obtain reproducible and representative results [12, 13]. The samples were introduced into polyethylene bags, to avoid contamination and loss of moisture and then sent to the laboratory in less than 10 h to keep field conditions as steady as possible.

Data on environmental temperature and moisture were measured during sampling.

Moisture content of the samples was determined as the mass loss after treatment in oven [14, 15]. All the samples were sieved at 2 mm and then placed in hermetically closed polyethylene bags and left in the laboratory at 4 °C. The elemental composition was determined in the laboratories of the Elemental Analysis Service of Santiago University.

### Differential scanning calorimetry

Firstly, the samples of soil were dried in an oven to 80 °C for up to 4 h. DSC curves of dry soil samples were carried out using a Differential Scanning Calorimeter (DSC-2910 TA-Instruments) and replicated three times. These DSC curves were obtained under a dry air flowing at 110 $cm^3\ min^{-1}$ and a scanning rate of 10 $°C\ min^{-1}$, and using samples between 10 and 30 mg of soil into open aluminium pans. The range of temperatures studied was between 50 and 600 °C.

The ignition temperature and the heat of combustion ($Q$) of dry soil (in $J\ g^{-1}$ dry soil) were measured directly from the DSC curves. This method was widely described in previous papers [4, 10]. The loss of sample mass ($\Delta m$) as consequence of the organic matter combustion inside the calorimeter was calculated and the heat of combustion of the organic matter ($Q'$) could be then determined (in $J\ g^{-1}$ of O.M.) using: $Q' = \frac{Q\, m_s}{\Delta m}$, where $m_s$ is the sample mass before the DSC analysis.

## Results and discussion

Figure 1 shows the DSC curve of a sample of arable soil. It has the typical profile of the DSC curves of the samples of this work, which are characterized by three well defined peaks.

The first peak is endothermic and it is provoked by the loss of water and volatile substances.

The second peak, exothermic, is due to the thermally induced oxidation of the soil organic components, taking place between 220 and 550 °C approximately. This peak can be considered as the overlapping of two exothermic reactions from the decomposition and combustion of different organic matter components with distinct and contrasting thermal stability, the first one (exo1) presents a minimum at 320 °C approximately, attributed to decomposition of more thermolabile compounds, basically aliphatic structures, such as cellulose, holocellulose, fulvic acids and simple sugars and decarboxylation of carboxylic groups [11]. The second one (exo2) presents the minimum between 380 and 400 °C, due to decomposition of less thermolabile material, mainly aromatic components, such humic acids and lignin [11].This second peak is lower than the first, appearing rather as a shoulder, instead of a peak.

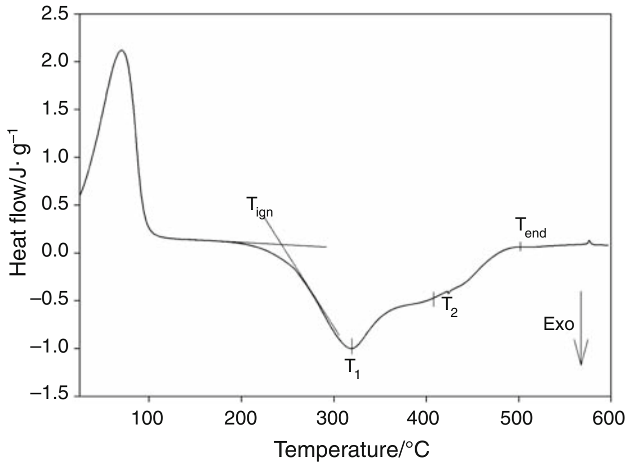


**Fig. 1** DSC curve of a sample or arable soil before dehydrating. The three main peaks and the temperatures that combustion starts ($T_{ign}$), exo1 ($T_1$), exo2 ($T_2$) and end of combustion ($T_{end}$) are shown

The last peak, endothermic, is due to the polymorphic transformation of the quartz [10].

Figure 2 shows the DSC curves of arable and pine wood soils in the different seasons, to be easily compared. The labile fraction of the organic matter is a major proportion in the recalcitrant one of all the samples studied. Differences between the profiles of these DSC curves for both soils are clear except in winter, because in this season the microorganisms have a minimum activity and the similarity among both soils is revealed in these curves.

Figures 3 and 4 show the DSC curves of seasonal samples of arable and pine wood soils, respectively. Although the profiles are similar in both soils, some differences can be found in second soil, the exo2 peak is smaller in winter than in the other seasons. This fact implies that the combustion peak of the organic matter ends to minor temperatures than in the rest of the samples.

Tables 1 and 2 show the results of organic matter content (OMC), C to N ratio (C/N), pH, moisture, soil sampling temperature, heat of combustion per gram of dry soil ($Q$) and per gram of organic matter ($Q'$), ignition temperature ($T_{ign}$), temperatures of the minimum of the peaks ($T_1$ and $T_2$), temperature of the end of the peak of combustion ($T_{end}$) and temperature at which the energy released is half of the total stored ($T_{50}$) [2] obtained for the soils studied.

The values of pH correspond to the acidity of soils; as the main soils of this region, pine wood soil presented lower pH values in all the samplings, due to the addition of fertilizer in arable soil that increases this parameter.

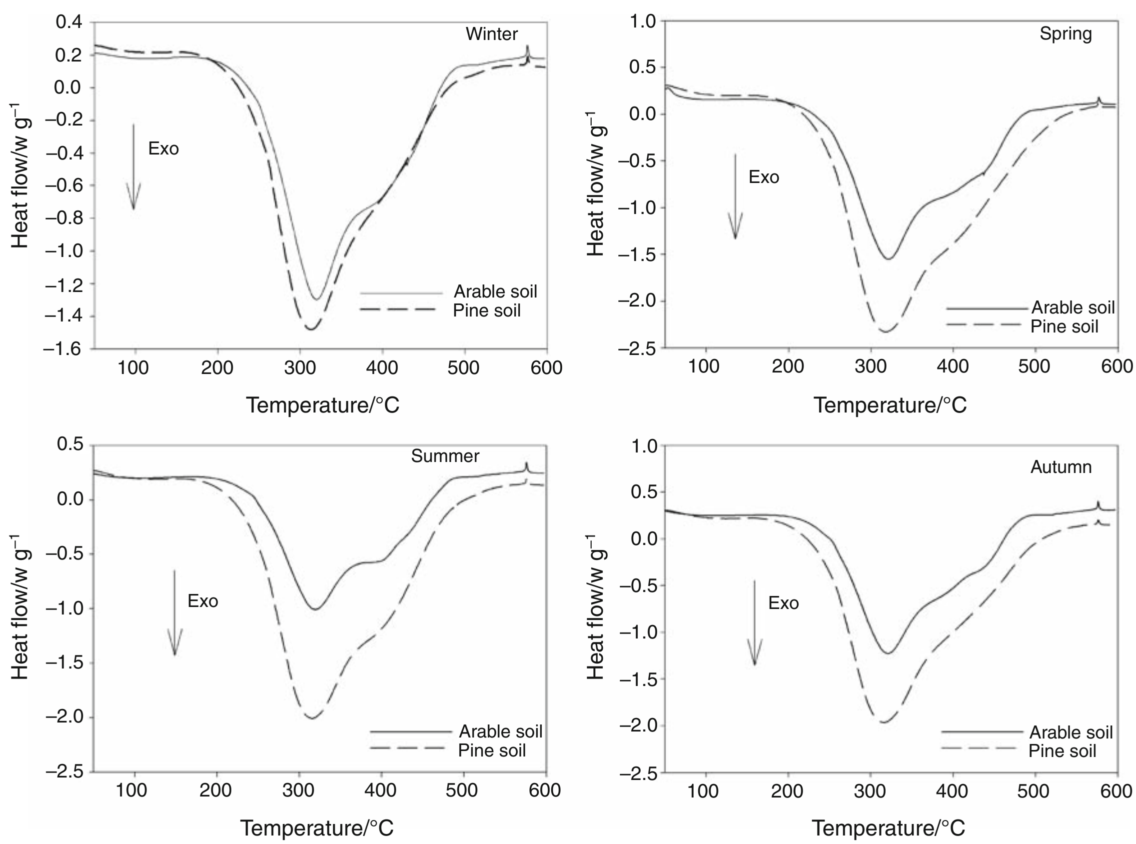


**Fig. 2** Comparison between the DSC curves of arable and pine wood soils for each season

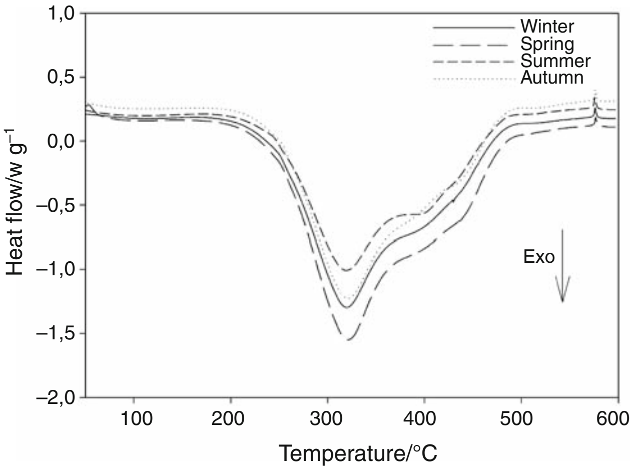


**Fig. 3** DSC curves of dehydrated samples of the arable soil

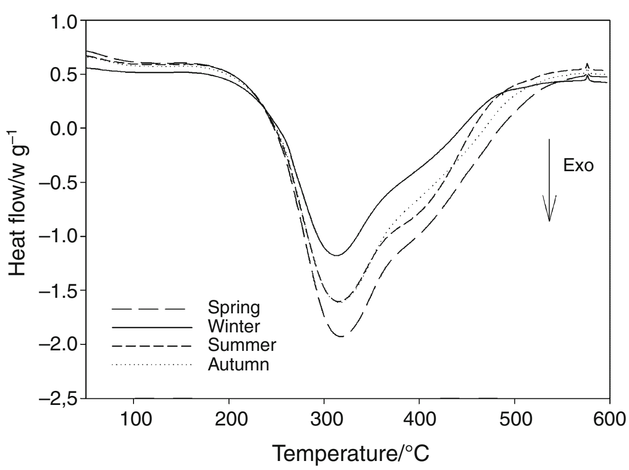


**Fig. 4** DSC curves of dehydrated samples of the pine wood soil

Fertilization of the arable land makes C/N relation better for productivity in that soil in spite of OMC being higher in the pine wood sample.

The moisture is almost constant and the soil temperature is less extreme in pine soil. Both parameters are directly related to OCM, because in soils the OM acts as a shock absorber system. In pine wood soil the OCM values are higher than arable soils. For this reason, its temperature and moisture are more stable during the whole year.

The heat released during the combustion per gram of dry soil presents similar values along the year in both soils except in pine wood soil in winter. The values of this property for arable soil are sensitively different (37% lower) than the corresponding in pine soil agreeing with the organic matter content, as it can be expected because both parameters are in highly significantly correlated [16, 17].

The values of heat released per gram of organic matter did not present seasonal variations, and the differences between arable and pine wood soils are lower than that of heat released per gram of soil. This fact reveals that in spite of both soils having the same nature, the different uses along last 15 years provoked changes in quantity and quality of organic matter.

The temperature of ignition, temperature of end of combustion and temperatures of maximum degradation of labile and recalcitrant components ($T_{ign}$, $T_{end}$, $T_1$ and $T_2$ in Tables 1 and 2), did not show seasonal variations in the two studied soils. Whereas, taking into account that the combustion interval (C.I.) is the interval between ignition and end temperatures, it can be observed that C.I. is higher in pine wood soil (239–560 °C) than arable soil (245–505 °C). This indicates that the distribution of organic matter is more complex in pine soil, existing more fresh organic matter associated to lower degradation temperatures and also more

**Table 1** Values of the organic matter content (OMC), C to N ratio (C/N), pH, moisture, soil temperature in the sampling, heat released during the combustion per g of dry soil ($Q$) and per g of organic matter ($Q'$), ignition temperature ($T_{ign}$), temperatures of exo1 ($T_1$) and exo2 ($T_2$) peaks and $T_{50}$ of culture soil

| | Winter | Spring | Summer | Autumn |
|---|---|---|---|---|
| OMC/% | 8.0 | 7.8 | 8.6 | 7.9 |
| C/N | 14 | 17 | 10 | 11 |
| pH | 5.9 | 5.5 | 5.8 | 5.6 |
| Moisture/% | 31.3 | 31.6 | 17.6 | 30.2 |
| Soil temperature/°C | 7.7 | 24.0 | 29.3 | 17.1 |
| $Q$/J/g dry soil | 1.18 ± 0.08 | 1.26 ± 0.09 | 1.14 ± 0.17 | 1.18 ± 0.03 |
| $Q'$/J/g M.O. | 8.5 ± 0.6 | 8.0 ± 0.5 | 8.2 ± 0.2 | 7.4 ± 0.5 |
| $T_{ign}$/°C | 244 ± 1 | 247 ± 1 | 244 ± 1 | 247 ± 1 |
| $T_1$/°C | 319 ± 1 | 320 ± 1 | 320 ± 1 | 321 ± 1 |
| $T_2$/°C | 400 ± 5 | 400 ± 5 | 397 ± 8 | 408 ± 6 |
| $T_{end}$/°C | 504 ± 5 | 510 ± 4 | 500 ± 6 | 500 ± 4 |
| $T_{50}$/°C | 340 ± 1 | 341 ± 1 | 340 ± 2 | 340 ± 2 |

**Table 2** Values of the organic matter content (OMC), C to N ratio (C/N), pH, moisture, soil temperature in the sampling, heat released during the combustion per g of dry soil ($Q$) and per g of organic matter ($Q'$), ignition temperature ($T_{ign}$), temperatures of exo1 ($T_1$) and exo2 ($T_2$) peaks and $T_{50}$ of pine wood soil

| | Winter | Spring | Summer | Autumn |
|---|---|---|---|---|
| OMC/% | 7.2 | 12.6 | 13.0 | 11.0 |
| C/N | 22 | 22 | 17 | 19 |
| pH | 4.7 | 4.5 | 4.5 | 4.3 |
| Moisture/% | 28.6 | 31.4 | 20.4 | 30.9 |
| Soil temperature/°C | 9.0 | 23.5 | 28.1 | 14.8 |
| $Q$/J/g dry soil | 1.43 ± 0.04 | 2.08 ± 0.23 | 2.02 ± 0.06 | 2.04 ± 0.13 |
| $Q'$/J/g M.O. | 9.7 ± 0.5 | 9.7 ± 0.2 | 10.9 ± 0.3 | 10.1 ± 0.4 |
| $T_{ign}$/°C | 239 ± 3 | 239 ± 1 | 238 ± 1 | 239 ± 1 |
| $T_1$/°C | 311 ± 2 | 316 ± 2 | 316 ± 2 | 317 ± 2 |
| $T_2$/°C | 409 ± 4 | 425 ± 7 | 405 ± 5 | 410 ± 5 |
| $T_{end}$/°C | 550 ± 5 | 560 ± 4 | 565 ± 6 | 560 ± 5 |
| $T_{50}$/°C | 334 ± 2 | 345 ± 2 | 342 ± 2 | 343 ± 2 |

evolved or recalcitrant organic matter which degrades at higher temperatures. The fact that the C.I. is major in the pine soil agrees with that the values of organic matter content and the heat of combustion are also major in this soil.

The temperatures of maximum degradation of labile and recalcitrant components of organic matter are 320 and 400 °C, respectively, in arable land and 316 and 410 °C in forest soil, although this last temperature presents more variations than the other three, raising 425 °C in samples of spring. The differences between $T_1$ and $T_2$ are higher in pine wood soil than arable soil in all the samplings, indicating a bigger resolution peak, which indicates that labile and recalcitrant fractions of organic matter are more differentiated in forest soil.

$T_{50}$ is lightly lower in culture than in forest soil and in both of them this parameter is practically constant along the year, except in samples from pine wood soil taken in winter, probably due to the fact that the decomposition of fallen leaves and fallen branches during the autumn took place, increasing the proportion of labile organic matter. In general terms, that means that the stored energy is more available (it needs less energy input to be released) in arable soil than pine wood soil.

## Conclusions

The DSC is a suitable tool to provide additional information about the stabilization of SOM from the temperatures and shapes of the peaks associated to the labile and recalcitrant components.

Thermal properties of arable soil did not show seasonal variations due to the human control. Minimum values of organic matter content, heat released during combustion per gram of dry soil and $T_{50}$ have been found in pine wood soil sampled in winter, although these properties showed similar values in the other three seasons.

Fifteen years is a small period of time to find clear differences in DSC profiles of soils with similar nature but pine wood soil presents several indications to have the most complex and stabilized organic matter with regard to arable land, as an increase in the organic matter content, decrease of the ignition temperature, major ending temperature of combustion peak, exo1 and exo2 peaks more resolved and major $T_{50}$ temperature. Therefore these thermal parameters can be introduced as a numerical indicator of the availability of O.M. and related with the recalcitrance and degree of stabilization of the organic matter.

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