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Calorimetric seasonal characterization of culture and pasture soils

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Abstract Isothermal and Differential Scanning Calorimetry is applied to analyze the evolution of soil using its microorganisms and organic matter as bioindicators of soil quality. This study was carried out with two similar soils under different agricultural activities: culture and pasture. Sampling and measurements were performed through 1 year in order to check the sensitivity of common calorimetric indicators of microbial activity and organic matter to the different climatic seasons in the sampling place: spring, summer, fall and winter. Results show that these indicators are sensitive to changes related to climatic conditions but the variability depended also on the nature of the soil: pasture or agricultural land. The results achieved through the present study show that the procedure here proposed could be used on any soil everywhere, providing the determination of the own parameters of soil and zones.

Keywords Soil · DSC · TAM · Biomass · Organic matter · Seasonal variations

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Introduction

The Kyoto Protocol on Climate Change in 1997 demands the understanding of the behaviour of soil carbon dynamics, because de amount of soil organic matter represents one of the largest reservoirs of organic carbon on the global scale [1]. The annual rate at which the organic matter is lost can vary greatly, depending on cultivation practices, the type of plant cover, drainage status of the soil and weather conditions [2] and consequently, the soil exploitation must be under control. That is one of the main reasons why the Kyoto protocol advocates also for the introduction of new technologies to provide that control in a reliable, rapid and slightly destructive way. In this sense, different research groups have been working with calorimetric techniques in different soil research areas to give solid bioindicators of soil quality [3–6], informing about the impacts on the soils, as forest fires in N.W. of Spain [7–9]. This information can be given by calorimetry very fast and can contribute to the sustainable development of the soil system.

For these reasons is important to settle the role of calorimetry in soil research. One of the ways is by checking the sensitivity of the calorimetric indicators of microbial biomass and organic matter to the physic-chemical and environmental properties of the soil. Heterogeneities and discontinuities in the physic-chemical environment are a hallmark of soil systems with the obligation for soil microbes to adapt the metabolism [10]. The proposed calorimetric indicators in this paper have been applied in soil research [11–13], but curiously very few publications report about their sensitivity to detect metabolic activity and organic matter changes have been found [14, 15]. There is also a complete lack of information about the sensitivity of the calorimetric indicators to seasonal changes. The goal of this paper is to show how the

environmental changes associated to different seasonal climatic conditions affect to two of the most important indicators of soil quality: biomass and organic matter, given by isothermal calorimetry and DSC.

Materials and methods

Sampling

Soil samples from two soils located in Viveiro, Galicia, NW Spain, were collected during one 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 is a Pasture soil.

For collection of these samples, 100 m^2 of a land area were chosen and divided into 1 m^2 sites, six of which were randomly chosen after eliminating those situated in the borders [13]. 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 [16, 17]. 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 avoid loss of moisture and thus keeping field conditions as steady as possible.

Data on environmental temperature and moisture were measured during sampling.

Laboratory sample preparation

Once in the laboratory, moisture content of the samples was determined by thermogravimetry.

Samples were sieved and then placed in hermetically closed polyethylene bags and left in the laboratory at 4 °C for up to 3 months to ensure reproducibility of measurements before being used for the calorimetric experiments [18].

Elemental composition

The determination of organic matter content and the C-to-N ratio, C/N, has been done. The C/N ratio is basic for determination of the mineralization degree of soil, and the organic matter content gives information about the capacity of a soil to supply nutrients to the living phase in it for a correct development [19]. Total nitrogen was determined by Kjeldahl method. The elemental composition was determined in the laboratories of the Elemental Analysis Service of Santiago University.

Isothermal calorimetry

Calorimetric experiments were performed using a microcalorimeter 2277 Thermal Activity Monitor (TAM) Thermometric AB. Measurements were carried out in hermetically sealed 5 mL stainless steel ampoules. Soil samples of 1 g size at water-holding capacity were treated with 1.25 mg of glucose. Experiments were repeated four times. The reference ampoule was filled with 1 mL of distilled water. The soil microbial activity due to the glucose addition is given as power–time curves. Integration of these curves provides values of the total heat evolved by that process, Q_T. The direct analysis of these curves also yields the evolution of the Peak time (Pt), which is the time to reach the maximum value of the peak, the value of the Peak height (Ph), which is the power at the maximum of the peak, and the microbial growth rate constant, μ [13, 18, 20].

Differential scanning calorimetry

DSC curves of the soil samples were carried out using a Differential Scanning Calorimeter (DSC-2910 TA-Instruments) and replicated six 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}, a 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 heat of combustion and the ignition temperature of the soil organic matter were calculated directly from the DSC curves of the dry soil. These parameters provide us information about the potential of thermal degradation of the soils. This method was widely described in previous papers [7, 8, 21].

Results and discussion

Figure 1 shows the power–time curve of the pasture soil in summer. It follows the typical pattern associated to a microbial growth reaction which is very common in soils when they are amended with an easily degradable external C source as glucose [18]: a small lag phase, less than 5 h, an exponential growth phase from 5 to 20 h, followed by a very short steady phase. The power–time curve declines to a new stationary metabolism 25 h after the beginning of the calorimetric measurement, characterized by a balance between the dead and alive microorganisms due to the exhaustion of the external carbon resource.

Figures 2 and 3 show the power–time curves obtained for the culture and pasture soils during the different seasons. The ANOVA of the tabulated data gave significant differences among the samples and among the different seasons

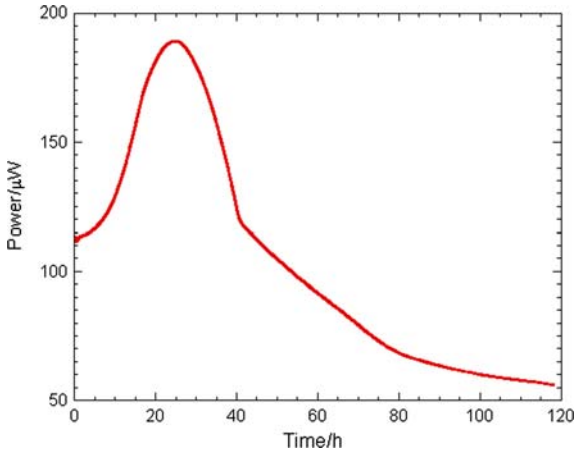

Fig. 1 Typical power–time curve from TAM

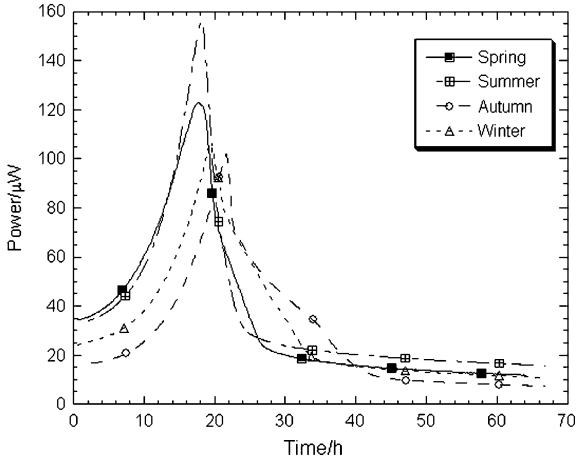

Fig. 2 Power–time curves of every season of culture soil

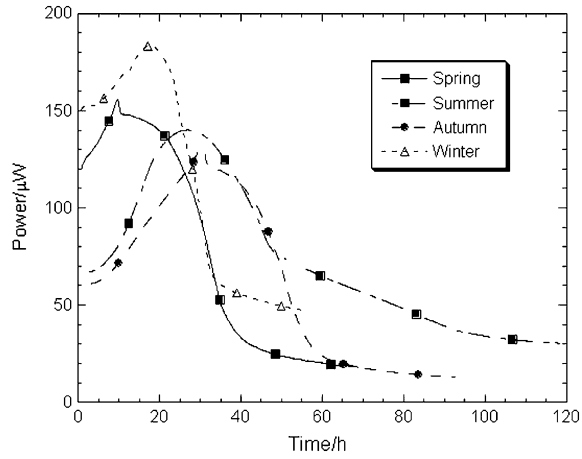

Fig. 3 Power–time curves of every season of pasture soil

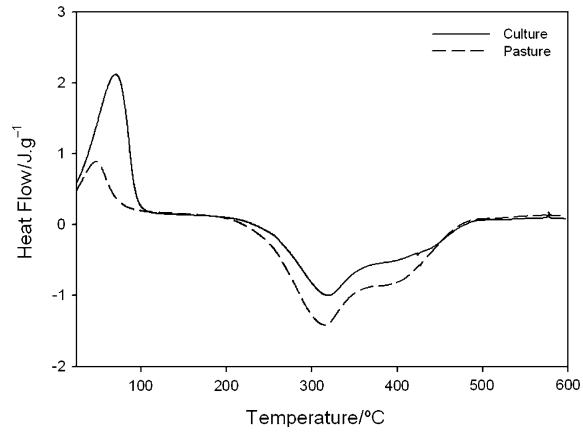

Fig. 4 Comparison of the DSC curves of culture and pasture soil sampling in spring

suggesting metabolic adaptations to the environment. In the pasture soil, the values of peak time are different, ranging from 8.75 to 30.71 h in spring and in autumn, respectively. The reason could be attributed to differences in the initial quantity of biomass that is activated by the glucose. That is given by the heat rate during the lag phase [22, 23]. It can be observed in Figs. 2 and 3 that the heat rate during the lag phases is different. Moreover, culture soils reach the new stationary metabolism before than pasture soils (40 and 60 h, respectively).

Figure 4 shows, as example, the DSC curves of both soils sampled in spring which present three well defined peaks, the first one is endothermic and is provoked by the loss of water and volatile substances, the second peak, exothermic, due to the combustion of the soil organic matter, taking place between 220 and 570 °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 (Exo 1) presents a minimum at 320 °C approximately, attributed to decomposition of more thermolabile compounds, basically aliphatic compounds, such as cellulose, holocellulose, fulvic acid and simple sugars; whereas the second one (Exo 2) presents the minimum between 380 and 400 °C, due to decomposition of less thermolabile material, mainly aromatic components, such humic acids and lignin. The last peak, endothermic, is due to the polymorphic transformation of the quartz [21].

Figure 5 shows the DSC curves of all the samples of culture soil. Theses samples were previously dehydrated in an oven at 100 °C during 2 h, being that the reason why the first endothermic peak is not present. Figure 6 shows the DSC curves of all pasture soils samples. All the DSC curves showed a shoulder at temperatures corresponding to Exo 2, more than a peak in strict sense, suggesting that the aliphatic components are in major proportion than the aromatics in all the samples in both soils, being in agreement with the main components of the vegetation that normally cover these soils, corn, bean and grass are poor in lignin.

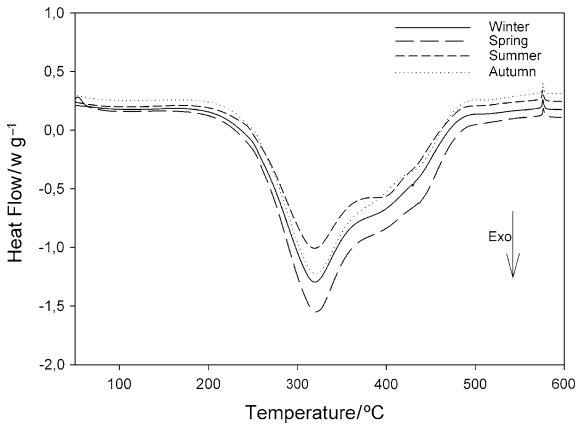

Fig. 5 DSC curves of dehydrated samples of the arable soil

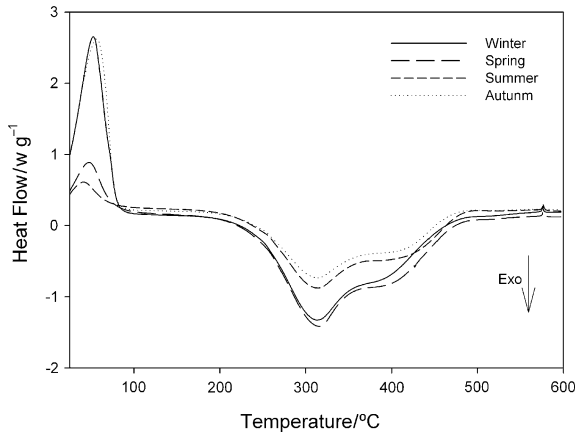

Fig. 6 DSC curves of seasonal samples of the pasture soil

Tables 1 and 2 compile the main values of the parameters determined from these curves as well as the values of the organic matter content and the relation C/N. These results were obtained from DSC and TAM experiences. In these tables, it can be emphasized that:

- No significant differences in all the parameters (peak time, peak height, or total heat evolved during the processes) of the four samplings of culture soil have been found, except in the C/N ratio. These values are constant along the year because arable soil was under human "control". That makes this land less sensitive to the changing climatic conditions (temperature and humidity). The values of all the parameters in the pasture soil are not as stable as the arable land. It seems this soil is more affected by the climatic regime in the sampling location.
- Although relations C/N are very similar, they are more stable in the pasture soil. The most suitable value of C/N is that obtained in summer in the arable land because during the late winter–spring the soil is fertilized, probably with organic fertilizers that alter the C/N ratio. On the contrary the pasture soil shows the less favoured C/N ratio in summer probably because it coincides with the highest vegetable growing rate that may deplete the soil N levels.
- The organic material content is practically constant for culture soils along the year due to the continuous addition of manures, whereas pasture soil presents seasonal variations.
- The heat of combustion of the organic matter and the organic matter content of the pasture soil presented the lowest values in summer and autumn, coinciding in these seasons with the highest values of the heat released by the microorganisms. Due probably to that in winter the microorganisms are in a semi-latent state as a consequence of the climatic conditions, whereas with the increase of temperature in the late spring, the microorganisms start to degrade the organic matter, which decreases as a consequence of the microbial activity in summer and fall.
- Values of total heat evolved during the processes, Q_t, are higher for pasture soils than for the arable land. The pasture also shows a higher heat rate during the lag phase than the arable land. Then, the high values of Q_t

Table 1 Values of the organic matter content (OMC), C to N ratio (C/N), peak time (Pt), peak height (Ph), total heat (Qt), partial Heat (Qp), microbial growth rate constant (μ), heat of combustion (Q), ignition temperature (T ign) and temperature of the minimum of the combustion peak in DSC curves of culture soil

	Winter	Spring	Summer	Autumn
OMC (%)	8.0	7.8	8.6	7.9
C/N	14	17	10	11
Pt (h)	19.2 ± 0.6	18.3 ± 0.6	18.7 ± 0.9	21.0 ± 0.9
Ph (μW)	106 ± 4	122 ± 5	157 ± 7	114 ± 5
Q_t (Jg^{-1})	3.35 ± 0.08	3.31 ± 0.02	3.28 ± 0.07	3.79 ± 0.05
Q_p (Jg^{-1})	1.70 ± 0.03	2.13 ± 0.03	2.26 ± 0.08	1.60 ± 0.02
μ (h^{-1})	0.107 ± 0.003	0.088 ± 0.002	0.106 ± 0.005	0.112 ± 0.001
Q (J/g)	1.18 ± 0.08	1.26 ± 0.09	1.14 ± 0.17	1.18 ± 0.03
T. ign (°C)	244 ± 1	247 ± 1	244 ± 1	247 ± 1
T min (°C)	319 ± 1	320 ± 1	320 ± 1	321 ± 1

Table 2 Values of the organic matter content (OMC), C to N ratio (C/N), peak time (Pt), peak height (Ph), total heat (Qt), partial Heat (Qp), microbial growth rate constant (μ), heat of combustion (Q), ignition temperature (T ign) and temperature of the minimum of the combustion peak in DSC curves of pasture soil

	Winter	Spring	Summer	Autumn
OMC (%)	11.8	9.5	7.9	7.0
C to N ratio	12	11	17	12
Pt (h)	17.9 ± 0.4	8.8 ± 0.3	25.2 ± 0.7	30.7 ± 0.8
Ph (μW)	185 ± 3	153 ± 3	144 ± 4	133 ± 3
Q_t (Jg^{-1})	2.25 ± 0.08	5.35 ± 0.18	1.56 ± 0.17	8.38 ± 0.26
Q_p (Jg^{-1})	2.00 ± 0.01	0.84 ± 0.03	3.77 ± 0.10	3.99 ± 0.02
μ (h^{-1})	0.0192 ± 0.0004	0.0122 ± 0.0001	0.0378 ± 0.0009	0.0356 ± 0.0007
Q (J/g)	1.75 ± 0.03	1.45 ± 0.47	1.01 ± 0.13	0.98 ± 0.21
T. ign (°C)	243 ± 3	239 ± 1	237 ± 1	236 ± 1
T min (°C)	314 ± 1	317 ± 1	316 ± 1	313 ± 1

could be attributed to the higher microbial biomass in the pasture than in the arable land.

- Values of Q_t for the arable land are also constant through the year suggesting a very stable microbial population also. On the contrary, the values of Q_t in the pasture vary depending on the season, indicating a microbial biomass sensitive to the climatic changes and an adaptation of the microbial metabolism to the different climatic seasons.
- Peak height values, P_h, are higher for the pasture also, in agreement with the highest active initial biomass in this soil. Arable land also shows a very stable value of microbial growth rate constant (μ) through the seasons, in agreement with the observed stability in the Q_t values while the μ value in the pasture is a sensitive parameter that shows a clear increase in the summer and fall, in agreement with the observed Q_t values and the observed trend in the organic matter content and the heat of combustion. It is clear that the manipulation of the arable lands for agriculture production makes that soil less sensitive to the environmental changes. On the contrary the pasture responds to the different seasons showing a clear depletion of the parameters linked to the quantity and nature of the organic matter when the parameters associated to the microbial activity increase. That happens in summer and fall in the pasture soil while winter and spring depletes the microbial activity favouring the accumulation of the organic matter during that period. The proposed parameters can show clearly these trends.

Conclusions

Calorimetry (TAM and DSC) is a suitable tool for the study of microbial activity in soils.

The proposed parameters are sensitive enough to detect changes in the microbial metabolism and in the quantity and nature of the organic matter caused by the climatic seasons. The adaptation of the metabolism is responsible for arising or depleting the quantity of the organic matter. It can be detected in soil with no human manipulation. The control of the arable land to keep the production makes the soil less sensitive to the environmental changes showing very stable values of the parameters linked to the microbial activity and organic matter through the year.

Calorimetry is a very useful method for continuous control of the soil since it permits to detect changes associated to the biomass and organic matter, easily, ecologically and fast. So, calorimetry shows as a very reliable method to assess microbial activity in soils. The main advantage of calorimetry over the other techniques is based on the continuous monitoring of soil microbial activity that provides a real and direct information that leads to productivity potential determination.

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