Sensitivity of thermal analysis and calorimetry to assess the impact of forest management on soils

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Abstract

Thermal analysis and calorimetry are useful tools for soil research providing different indices enriching the understanding of soil processes. In this work, we test their sensitivity to study the impact on soil of macroscopic forestry managements applied to eucalypt forest in the northwest of Spain: clearing scrub and thinning. Their impact on soil is assessed by differentiating the thermal properties of the organic matter and the biodecomposition. Thermal properties yield the percentage of soil organic matter, the heat of combustion and the degree of reduction of the organic matter.

Calorimetry provide the biodecomposition rates as the heat rate and the respiration rate by a calorespirometric procedure. These properties were determined to soils from different depths and tracked from young to mature forest stands under management and compared to their respective references. All of them were sensitive to the different forestry practices. Clearing and thinning caused losses of SOM due to enhanced microbial respiration in soils from sites, where the organic matter evolves to a more oxidized state from young to adult stands. These methods also allowed us discerning mechanisms making the organic matter to evolve to a more reduced or to a more oxidized state with time and with depth, suggesting that natural evolution of the soil organic matter can depend on external factors like the land use and land use changes.

Keywords Thermal analysis · Calorimetry · Soils · Forest management · Clearing · Thinning

Introduction

Soil is one of the essential primary resources on earth being for that reason legislated for sustainable use. That involves a continuous study of best practices to maintain the soil conditions in an optimal fertility status [1]. This is challenging due to the complex chemical and biological nature of the soil organic matter, SOM, formed by a conglomerate of labile material bonded to mineral-stabilized molecules with varying reactivity affecting biodegradability, also influenced by local and global environmental and climatic issues [2, 3]. This complexity of SOM is responsible for coexisting procedures to unravel the SOM chemical composition, the role of SOM nature on bio decomposition and the sensitivity to different soil ecosystem management [4, 5].

Thermal analysis and calorimetry are tools providing additional information about soil chemical and biological properties that contributes to deepening in knowledge and understanding about the role of different soil fractions on SOM turnover [6, 7]. These methods are opening, as well, new perspectives to apply to soil research [8, 9]. The versatility of these procedures makes them suitable to be applied to the main soil research goals and to be in continuous evolution within the soil research for that reason. The goal of this work is to test their sensitivity to assess the impact of different macroscopic forest managements on soil, by considering the SOM nature and biodegradability and not only the impact on the C and SOM contents. These studies are of interest because soil management have an increasing importance in preserving forest ecosystems, in special in the context of this era struggled by extreme climate conditions threatening the conservation of forests on earth.

This study took place in the northwest of Spain, where most of eucalyptus forest management focus on cellulose and sawn production for industry. Rotations for the species *Eucalyptus nitens* Deane & Maiden range between 12 and 20 years if the stands are intended for cellulose, and 25 years for saw wood. Thermal analysis and calorimetry contributed to settle the role of the rotation times of forests in the region on the SOM nature and soil capacity to keep the carbon, C, [10, 11] demonstrating how short rotations affect to the quantity and nature of C and SOM.

Further than rotation time, the main treatment carried out on these stands is the clearing of the scrub to control the vegetation in the initial stages of the rotation to avoid competition, and at more advanced ages, to break the horizontal and vertical continuity of fuels to prevent the spread of fire. Another treatment that is only carried out in the case of sawn wood is thinning, which can be systematic or semi-systematic until reaching 150–200 plants per hectare after 6–9 years [12]. The possible effect of these treatments on soil has not been tested yet.

Here, the effect of clearing and thinning on soil properties is studied by elemental, thermal and calorimetric analysis and compared to those from eucalypt forest references, where those managements did not take place. The possible impact on soil is studied by changes in the CHN composition, on the SOM quantity, and on the heat of combustion linked to the degree of reduction of SOM [13–15], to link the impact of the forest management to changes in the SOM chemical nature. SOM biological properties were analysed by the calorimetric monitoring of the microbial metabolism responsible for SOM decomposition by a calorespirometric procedure giving the rate of the soil microbial respiration by the CO2 released, and the total microbial metabolic rate by the heat rate, Rq. Both indices, CO2 and heat rate, are a measure of the SOM biodegradation rate [16] and have been proved to be sensitive to different soil ecosystems [9, 17].

Material and methods

Soil samples and sampling sites

Soil samples were collected in NW of Spain (Lugo, Galicia) and no more than 10 km apart from each other. All of them correspond to eucalypt forests (*Eucalyptus nitens* Deane & Maiden). Eight plots have been selected, following age criteria (young, medium age and adult) and looking for close replicas with and without management. The management treatments studied have been scrub clearing at three different ages and thinning at adult age. Clearings are generally carried out in a mechanized way along the streets of the plantation. The thinning that has been evaluated has been carried out systematically, eliminating four out of every five trees. The previous land use in the plots, was mainly forestry, according to existing orthophotos of earlier years. In most cases, the land was covered by trees for productive purposes (plantations), with only two plots dominated by shrubs in the past (Samples ACM and ASC, both adult forests without clearing and thinning respectively).

Collection of soils followed a depth gradient with SOM at different degrees of decomposition: LF representing the organic litter on the soil surface, and soil mineral layers from 5 and 10 cm from the soil surface. They were sampled at six specific points within the plots, as shown in Fig. 1, by a systematic sampling method consisting in the random selection of a point within the stand, close to its centre. Once this initial point is settled, six sampling points are chosen, maintaining an approximate horizontal distance of 5 m from the randomly selected point in the previous step (Fig. 1A). The first point is oriented in a northward direction (0°), with the subsequent points evenly spaced at 60° intervals in a clockwise direction (60°, 120°, 180°, 240°, and 300°). It's worth noting that the positions selected for sampling may undergo minor adjustments to avoid excessive proximity to trees or other elements that could potentially distort the nature of the sample.

At each sampling point, samples were taken following the depth gradient, distinguishing on the one hand the organic horizons (L/F) from the minerals, and within the minerals, two depths.

At each sampling point for the three depths (LF, 5, and 10), the collected samples were merged into a single sample per plot and placed in polyethylene bags for preservation. Approximately 125 cm^3 (in the form of a 5 × 5 × 5 cm cube) was taken as the minimum volume from each sampling point, to ensure that the combined sample from each plot and depth reached an approximate volume of 750 cm^3. These samples were stored in polyethylene bags at a temperature of 4 °C.

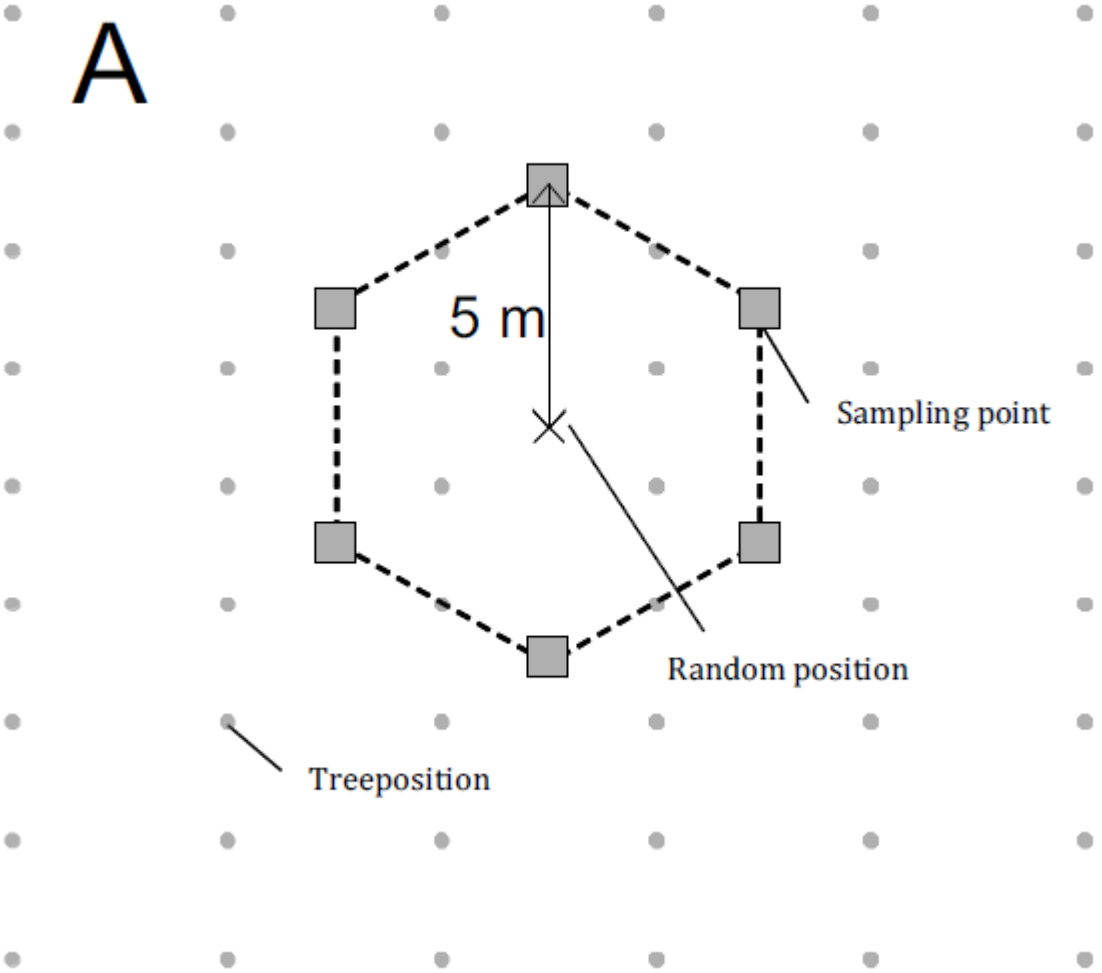


Fig. 1 Organization of soil sampling points

All mineral samples were sieved through 2 × 2 mm at humid conditions.

Soils for elemental and thermal analysis were dried in an oven at about 105 °C for 24 h to determine the water content by the gravimetric method [18]. Dry LF samples were also grinded to obtain homogeneous samples for the elemental and thermal analysis.

After sieving, samples for the calorimetric measurements were kept at their humidity conditions in polyethilene bags at 4 °C. Calorimetric measurements began about 1 month and half after sampling to let soil to stabilize after sieving.

Elemental and thermal analysis

Elemental composition of soils was done by an automated LECO CHN analyser. Thermal properties were studied by a simultaneous TG-DSC (TGA-DSC1 Mettler Toledo). Soil samples were placed in 100 mL aluminium pans under a dry air flow of 50 mL min^{-1} and at a temperature ramp from 50 to 600 °C for LF samples and from 50 to 1000 °C for mineral samples, both at a rate of 10 °C min^{-1} [15] after calibration following the instructions of the device.

TG traces were analysed to provide the SOM percentage of soil on dry basis, [19]. DSC gives the heat of combustion of SOM, Q_{SOM}, in kJ g^{-1} SOM, by normalizing the heat flow data in mW to the mg of SOM combusted and by subsequent integration of the DSC plot in mW per mg of SOM versus time in seconds, after manual adjustment of a base line. The integration of the DSC plot takes place between 180 and 600 °C for all samples to

be the range of temperature at which SOM is combusted [7, 20] at the temperature rate used [21]. The obtained heat of combustion is adjusted for the temperature and for the condensation of water by the Baraldi's correction [22] as explained in previous papers [23] and normalized to the C content as previously done for soils [15, 19] to give the enthalpy of combustion of SOM, $\Delta_c H_{SOM}$, in kJ mol^{-1} C, from which the degree of reduction of SOM, λ, is determined by the Sandler and Orbey correlation [15, 24].

Calorimetric measurements

Calorimetric measurements were done with a six channel TAM III calorimeter (TA Instruments Waters) following a calorespirometric procedure for parallel monitoring of the heat and CO2 rate from soil microbial metabolism.

For these measurements, 10 g of soil samples stored at 4 °C were stabilized inside polyethylene bags at the temperature of the measurements (25 °C) for 24 h. After that time, these samples were brought to 50% of their water holding capacity and stabilized at that water content for about three days inside polyethylene bags with a water container at 25 °C. Aliquots of about 0.8 g were introduced in the calorimeter inside 4 mL stainless steel ampoules. One ampoule contains a soil layer, and a second ampoule has the same soil layer with a 0.4 M NaOH inside a container (200 μL). The three soil layers from one site are monitored at the same time. By this experimental procedure the CO_2 rate captured by the NaOH is monitored continuously together with the heat rate of the soil microbial metabolism. To be able to compare these rates among the different soils, the heat rate and the CO_2 rate versus time plots are integrated as functions of time for 24 h to yield the heat rate in mJ g^{-1} d^{-1}, and the CO_2 rate in micromole CO_2 g^{-1} d^{-1} as explained in previous papers [8, 23]. The heat to CO_2 ratio is determined by the quotient of the heat and CO_2 integrated values to give the calorespirometric ratio, CR, for the different soils.

Statistics

Uncertainties considered for elemental and thermal analysis were 5% and 3% respectively. Calorespirometric measurements were done with soil duplicates, and values for the heat and CO_2 rates are given as the average and standard deviation (n = 2). Statistical relation among the different indices and soil properties are studied by Pearson's correlation. Comparisons of stands at different evolutionary state were done by the non-parametric Wilcoxon test.

Results

Evolution of soil elemental, thermal and biological properties with depth

Table 1 shows evolution of the soil elemental composition (CHN) and SOM within the samples. All of them have a clear trend of C, N, H and SOM data to decrease with increasing soil depth. C is significantly and highly correlated to N and H (n = 24; r = 0.974 and r = 0.994 respectively, $p < 0.0001$ in both cases) and SOM (n = 24; r = 0.994, p < 0,0001) indicating the strong bond of CHN data to the SOM composition. This is an essential requirement for unit conversion from grams to mol of C from the experimental data.

Table 2 shows the Q_{SOM} data obtained directly from the DSC-curves, the modified values after Baraldi's correction, and the enthalpy of combustion of SOM, $\Delta_C H^0_{SOM}$ after normalization to the C/SOM ratio (also in Table 2).

$\Delta_C H^0_{SOM}$ yield the degree of reduction of SOM, λ, by the Sandler and Orbey correlation [15]. Evolution of λ with depth can be seen in Fig. 2. There is a clear trend of λ to increase with depth with just a few exceptions. Table 2 also shows the atomic H:C ratio of samples which tended to increase with depth too. H:C and λ have a positive significant correlation (n = 24, r = 0.50, $p < 0.05$).

Sample name	Layers	Age	Management	% C	% N	% H	% SOM
JSM LF	LF	Young	With clearing	42,16	1,511	5,06	76,95
JSM 0–5 cm	0 a 5	Young	With clearing	9,12	0,484	1,79	18,67
JSM 5–10 cm	5 a 10	Young	With clearing	4,56	0,250	1,35	10,06
JCM LF	LF	Young	Without clearing	10,34	0,662	1,97	22,11
JCM 0–5 cm	0 a 5	Young	Without clearing	7,39	0,508	1,58	16,59
JCM 5–10 cm	5 a 10	Young	Without clearing	5,81	0,393	1,43	12,60
MSM LF	LF	Medium	With clearing	27,38	1,219	3,7	51,37
MSM 0–5 cm	0 a 5	Medium	With clearing	6,01	0,411	1,52	12,41
MSM 5–10 cm	5 a 10	Medium	With clearing	5,03	0,35	1,45	11,55
MCM LF	LF	Medium	Without clearing	28,63	1,342	3,96	58,25
MCM 0–5 cm	0 a 5	Medium	Without clearing	11,70	0,693	1,97	23,33
MCM 5–10 cm	5 a 10	Medium	Without clearing	8,23	0,495	1,61	17,53
ASM LF	LF	Adult	With clearing	26,40	1,051	3,46	50,82
ASM 0–5 cm	0 a 5	Adult	With clearing	5,26	0,289	1,31	9,44
ASM 5–10 cm	5 a 10	Adult	With clearing	5,08	0,254	1,27	9,12
ACM LF	LF	Adult	Without clearing	28,40	1,416	3,82	56,80
ACM 0–5 cm	0 a 5	Adult	Without clearing	8,43	0,570	1,67	22,55
ACM 5–10 cm	5 a 10	Adult	Without clearing	6,26	0,447	1,48	16,45
ASC LF	LF	Adult	Without thinning	33,43	1,276	4	63,53
ASC 0–5 cm	0 a 5	Adult	Without thinning	9,26	0,470	1,54	16,27
ASC 5–10 cm	5 a 10	Adult	Without thinning	5,01	0,293	1,15	9,71
ACC LF	LF	Adult	With thinning	16,35	0,718	2,33	28,11
ACC 0–5 cm	0 a 5	Adult	With thinning	11,09	0,542	1,77	19,95
ACC 5–10 cm	5 a 10	Adult	With thinning	7,57	0,417	1,43	15,41

Table 1 Results of the elemental analysis of the samples (CHN) and SOM percentage determined by TG

Evolution with depth of the SOM microbial decomposition rates is shown in Fig. 3. There is a clear decrease of the CO_2 and heat rates with soil depth in all samples. CO2 and heat rates were significantly correlated to the SOM percentages ($n = 24$; $r = -0.905$, $p < 0.001$; $r = -0.872$, $p < 0.001$ respectively) and in a lesser extent to λ ($n = 24$; $r = -0.522$, $p < 0.01$; $r = -0.567$, $p < 0.01$ respectively) and to the atomic H:C ratio ($n = 24$; $r = -0.816$, $p < 0.001$; $r = -0.802$, $p < 0.001$). Therefore, the microbial decomposition rates of SOM decreased with increased degree of reduction.

Figure 4 shows the CR data determined for all samples. CR data of mineral soil samples were lower than those of LF samples in all cases. Figure 4 compares the CR evolution with that of the enthalpy of combustion, $\Delta_C H^0_{SOM}$ values. CR in the mineral samples varied among sites but in general were lower than their enthalpies of combustion, indicating that these soils metabolize substrates from SOM more oxidized than the entire SOM molecule.

Sensitivity to temporal evolution of the eucalypt stands.

The indices representing SOM, used to compare their temporal evolution, were the SOM percentages of the stands and the λ. SOM is closely and significantly correlated to the soil elemental composition and λ is a direct function of the $\Delta_C H^0_{SOM}$ derived from Q_{SOM}. Therefore, interpretation of the evolution of λ and SOM percentages can be extended to the other indices. This evolution can be seen in Fig. 5 for the samples without and under management (with and without scrub).

The SOM percentage and λ are sensitive to the age of the stands. Wilcoxon test indicated significant differences among those values from the young to the adult states. Samples without management tend to store SOM, and therefore, C, in all soil layers, as the forest evolves from the young to the adult state. Samples under management, where scrub was cleared, show the opposite trend. The SOM tends to a more reduced state with increasing maturity of the stands when it is accumulated and evolves to a more oxidized state with increasing age in the stands when there is SOM losses.

Samples	Q_{SOM} /kJ g^{-1} OM	Baraldi's Correction /kJ g^{-1} OM	C/SOM	$\Delta_c H_{SOM}$ kJ mol^{-1} C	H:C
JSM LF	15,42	17,25	0,547	378	1,440
JSM 0–5 cm	16,81	18,64	0,488	458	2,354
JSM 5–10 cm	15,52	17,35	0,453	460	3,552
JCM LF	16,32	18,16	0,467	466	2,286
JCM 0–5 cm	15,91	17,75	0,445	478	2,562
JCM 5–10 cm	16,61	18,44	0,461	480	2,949
MSM LF	16,34	18,18	0,532	409	1,621
MSM 0–5 cm	16,26	18,10	0,483	449	3,036
MSM 5–10 cm	18,39	20,23	0,435	557	3,455
MCM LF	14,58	16,41	0,491	401	1,659
MCM 0–5 cm	16,21	18,05	0,501	432	2,020
MCM 5–10 cm	17,07	18,91	0,469	483	2,346
ASM LF	16,08	17,91	0,519	414	1,572
ASM 0–5 cm	15,95	17,78	0,557	383	2,984
ASM 5–10 cm	17,00	18,83	0,557	406	2,997
ACM LF	16,57	18,41	0,5	442	1,614
ACM 0–5 cm	16,52	18,35	0,373	589	2,375
ACM 5–10 cm	16,34	18,17	0,380	573	2,833
ASC LF	15,36	17,19	0,526	392	1,435
ASC 0–5 cm	16,89	18,72	0,569	395	1,995
ASC 5–10 cm	16,45	18,28	0,515	426	2,753
ACC LF	16,59	18,42	0,581	380	1,710
ACC 0–5 cm	16,53	18,37	0,555	397	1,915
ACC 5–10 cm	16,68	18,52	0,491	452	2,265

Table 2 Thermal data of soil samples showing the procedure to convert the direct integral of the DSC (Q_{SOM}) to the enthalpy of combustion of the soil organic matter, $\Delta_C H_{SOM}$ in kJ/ mol C. H:C is the atomic H to C ratio

Figure 6 shows the evolution of the biodecomposition rates and the CR. Samples under management (Fig. 6a) tend to diminish the rates with increasing age. Since these rates were correlated to the SOM content, the reason can be attached to the depletion of SOM and C. Samples without management (Fig. 6b) increase the rate of decomposition of the LF layer with the age of the stands, while the rates of the mineral samples keep stable if the adult stand is compared to the young one. CR values are more variable with age in the stands under management than in the stands without. Samples from the stands under management have very stable CR values in the LF layer, with values indicating metabolism of substrates more reduced than carbohydrates (higher than 460 $kJ^{-1}C$), with a trend to decay to values attached to more oxidized substrates than carbohydrates in the mineral samples, in special in the adult samples, following the observed evolution of SOM to a higher degree of oxidation with age.

Soils from the stands without management have very stable CR data, around the values given for carbohydrates, except for the mineral soils from the adult stand, with values indicating decomposition of substrates more reduced

than carbohydrates, following the observed evolution of their λ too. The deepest soil layer of the adult stand did not have respiratory activity.

Therefore, SOM changes their chemical and biological properties when the eucalypt forest evolves from a young to a mature state.

Sensitivity to forest management

The effect of all the forest managements on soil was studied by comparing the accumulative C per sampling site, the averaged λ, and the accumulative heat and CO_2 dissipated by the soils from the adult stands and contrasted to those from the young sites as references. Results can be shown in Fig. 7. There is a general trend to accumulate C when comparing the samples from the adult stands with those from the young sites (JSM and JCM without and with scrub respectively). Adult samples, where scrub was cleared (ASM) have less C than those, where scrub is preserved (ACM). The samples under thinning (ACC) show less C than those without thinning (ASC). The degree of reduction of the adult sample with scrub (ACM) is higher than that of the adult site, where scrub was cleared (ASM). Preservation of the scrub makes SOM to evolve to a more reduced state than that of carbohydrates (λ = 4), while the degree of reduction of SOM in the soils from adult stands without the scrub is lower than that of carbohydrates and that of the young stand. Thinning did not alter the degree of reduction of SOM.

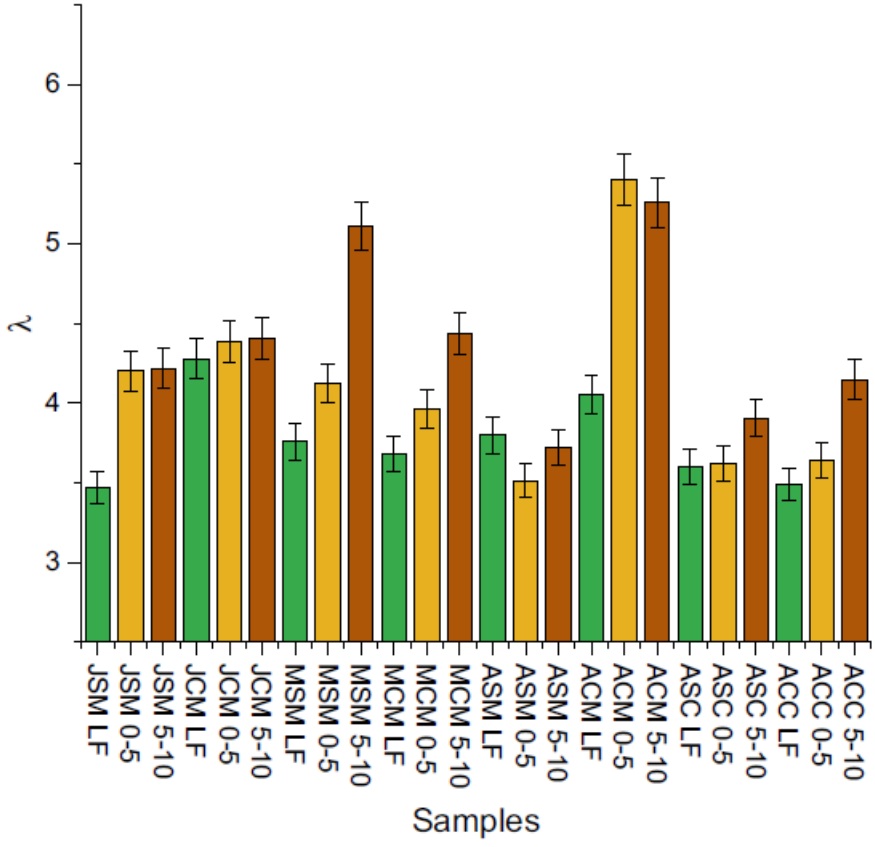
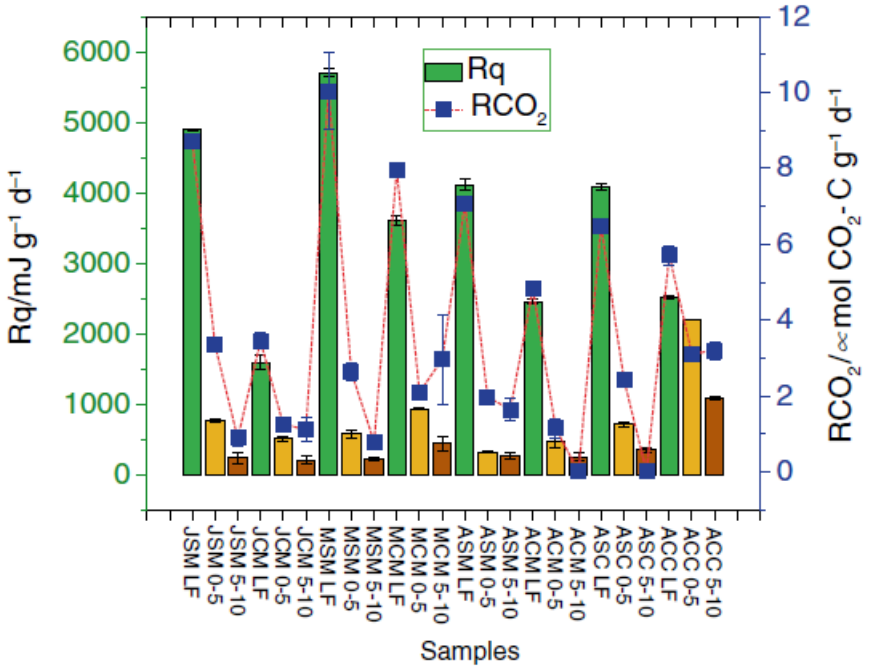


Fig. 2 Evolution of the degree of reduction of SOM, λ, for all samples used in this study. Reproducibility of thermal data is assumed to be 3%. Green is the LF layer, light brown the mineral soils from 5 cm depth, dark brown is the mineral soil from 10 cm depth. λ clearly increases with soil depth with the exception of samples JCM and ASM representing the young and adult stands with and without scrub respectively.



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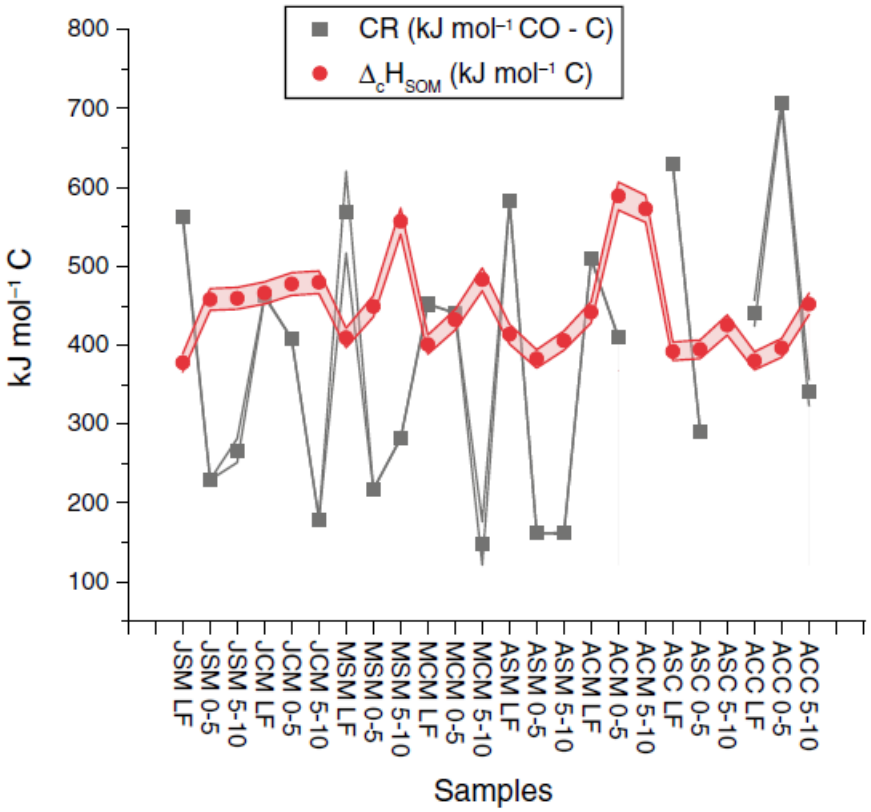
202 Fig. 3 Evolution of the soil microbial metabolic heat and CO_2 rates, Rq and RCO_2 respectively, in all the samples
203 of this study. Metabolic rates deplete with increased soil depth due to the decay of SOM and C percentages and to
204 the increased degree of reduction.



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206 Fig. 4 Evolution of the CR and $\Delta_C H_{SOM}$ of all the samples

It can be shown in Fig. 7b how the soil microbial metabolic rates varied among samples. Rq and RCO_2 rates values are both higher in the adult stands under management (clearing and thinning, ASM and ACC respectively) than those without (ACM and ASC). Higher respiration rates may be contributing to the lower C and SOM values in the adult samples under forest management. Respiration in the deepest soil layers is zero in all samples with scrub.

Evolution of CR showed that mineral soils from adult cleared forests (ASM) metabolize substrates more oxidized (162 kJ mol^{-1} CO_2–C) than those in soils from adult forests, where scrub is kept (ACM) (410 kJ mol^{-1} CO_2–C). CR was higher in the soil mineral layers of samples under thinning (ACC) (708 and 350 kJ kJ mol^{-1} CO_2–C from 5 and 10 cm respectively) than those without (ASC) (291 k kJ kJ mol^{-1} CO_2–C at 5 cm) showing inhibition of respiration in the deepest layer.

Discussion

The impact of forest management on soils is commonly assessed by tracking the evolution of the C stocks. In this paper it is introduced the SOM percentages, demonstrating to be as sensitive as the C to show different evolution attached to clearing and thinning practices. Nevertheless, their solely application as indicators for determining changes on the C stocks is under debate now [25, 26]. It has been recently reported that C measurements to assess impacts on C sequestration cannot result in climate change mitigation if the CO_2 release is not considered [25]. The CO_2 release can be mitigated by changes in the chemical nature of SOM. In this sense, results in this paper show how thermal analysis and calorimetry provide additional indicators to the quantitative measure of soil C, by monitoring the evolution of the SOM chemical nature through the heat of combustion and degree of SOM reduction, and by analysing SOM biodegradability by the heat and CO2 rates, yielding the CR too. All of them have been sensitive to prove changes on SOM nature in forest ecosystems under the different managements shown in this paper. The use of these indicators completes and enriches the information about the impact of those managements on SOM.

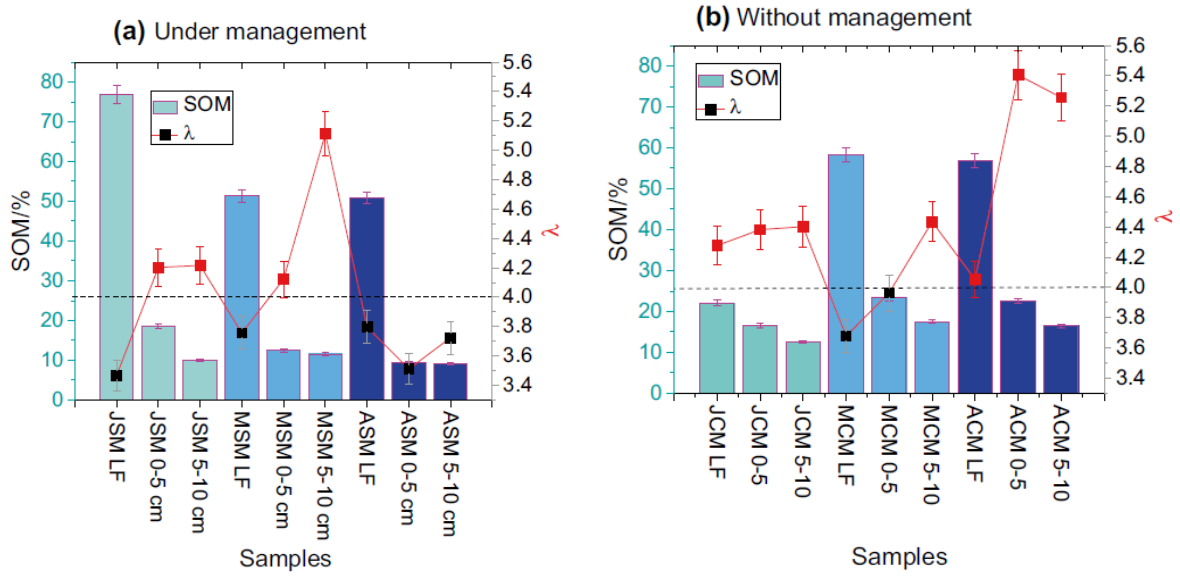
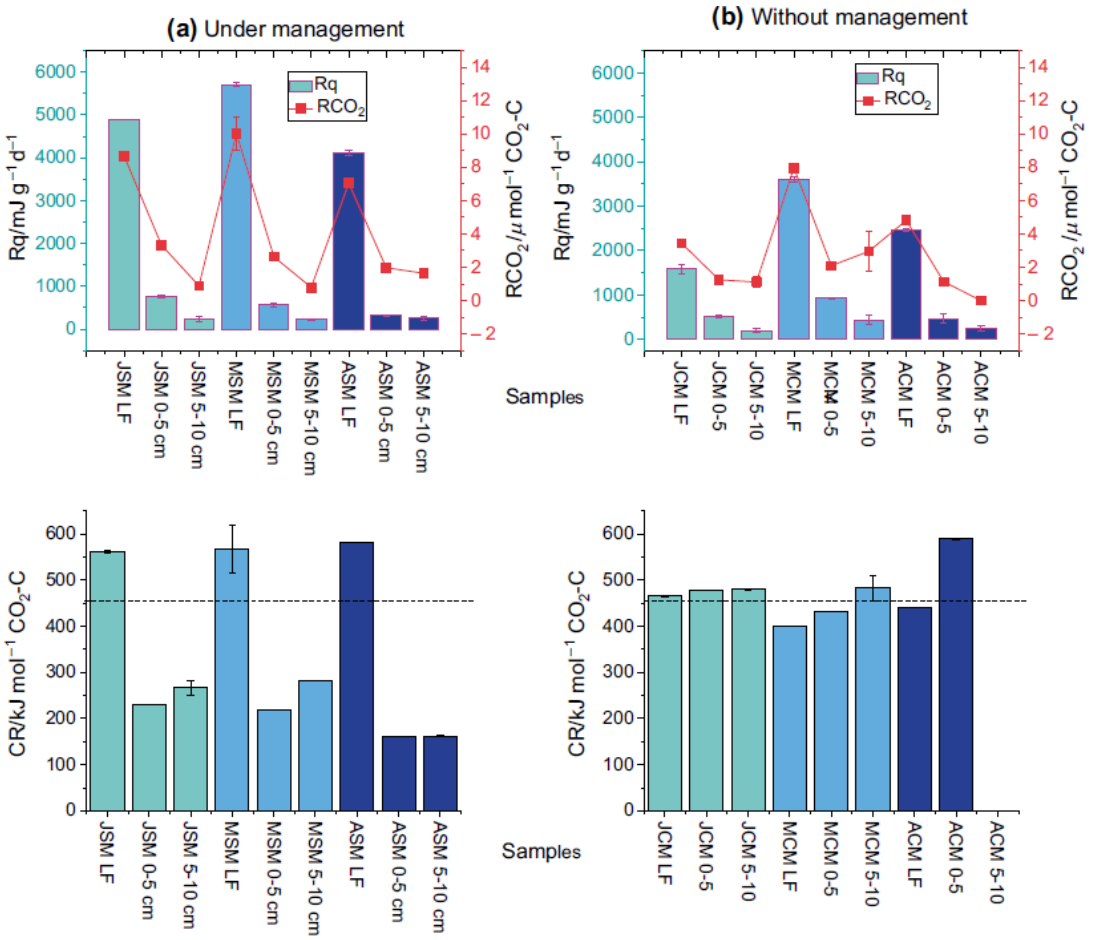


Fig. 5 Temporal evolution of the SOM percentages and degree of reduction, λ, of SOM from young to mature stands of eucaliptus under management (clearing of scrub, Fig. 4a) and without that management (Figure **b**). Bars from clear to dark blue represent the evolution of the SOM from the young to the mature stands. The dashed line shows the λ value for carbohydrates (λ = 4). Red points show λ values more reduced than carbohydrates and grey points the λ values more oxidized than carbohydrates



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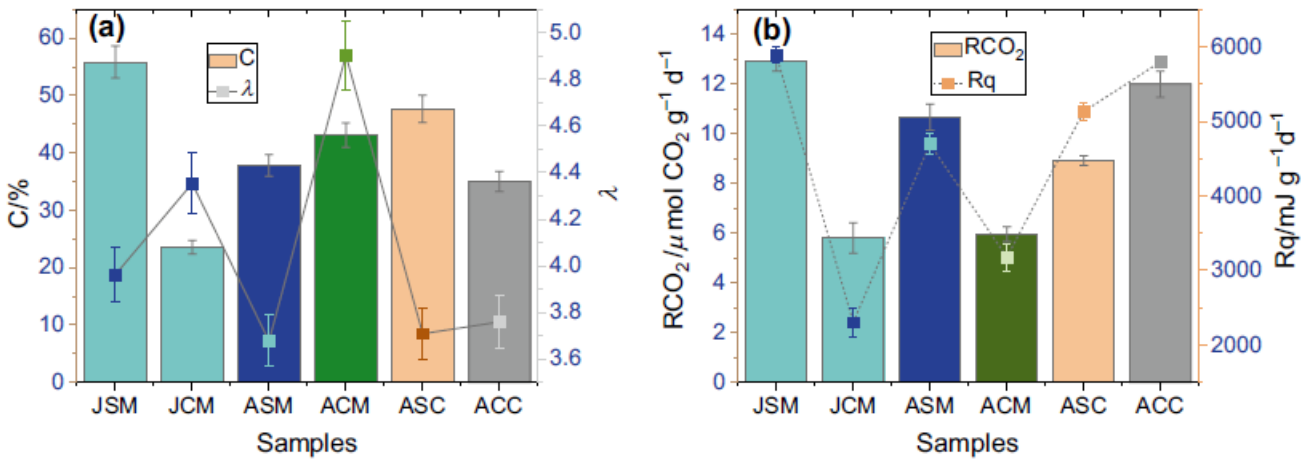
236 Fig. 6 Evolution of the soil microbial metabolic activity with the age of the stands. Bars from clear to dark blue
237 represent the evolution from young to mature sites for the heat rate and CR. Red points represent the respiratory
238 activity. The dashed line marks the CR value for carbohydrates.



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240 Fig. 7 This figure shows **a** the values for the degree of reduction, λ, and C %of the adult stands under different
241 managements. **b** have the data for the soil microbial metabolism of the same samples. Clear blue bars represent
242 the values for the young stands with (JSM) and without (JCM) management to be used as references. Different
243 colours represent different managements. Dark blue bars are the samples without scrub, the green ones represent
244 the sample with scrub, and light brown is the sample without thinning and the grey one under thinning.

Soil thermal and calorimetric properties settle the impact of scrub clearing on soil. Scrub contributes to C and SOM gain as the stands evolve from young to mature states. As SOM accumulates, it evolves to a more reduce state than that in the young sites, keeping the heat rates of soil microbial metabolism stable along with time, while soil microbial respiration decreases as the degree of reduction increased. In the region, where samples come from, soil is naturally stabilized by organic metal bonds with affinity to the carbohydrate fraction, making the labile SOM less available to microbial attack, which could explain the observed depletion in the respiration rates [27]. The presence of scrub may contribute to increase SOM λ values due to higher influence of material derived from roots which can be rich in chemical substrates more reduced than carbohydrates [28, 29]. This behaviour could explain the SOM and C gains from young to adult stands and it was observed in previous works studying evolution of SOM thermal and biological properties in different soil chronosequences [10, 11].

The clearing of the scrub completely altered the abovementioned trend in SOM evolution. The absence of scrub leads to SOM and C losses in the adult stands compared to the young ones, affecting to the SOM nature too, at a lower degree of reduction in the adult stands than that at the adult stands without management, indicating a clear trend to a more oxidized state. The respiration rates of the adult stands are higher than those in the samples without management and the CR values indicate metabolism of substrates more oxidized than those being metabolized in the adult's natural stands (without management). Literature report differing evolution of SOM nature attached to different soil types [30] but in this work the mineral soil properties derive from similar parent material (limestone and shale) [31] and all samples come from nearby places at similar environmental conditions, therefore the observed differences can be reasonably attached to the different forest management.

In the case of thinning, it appears to accelerate decomposition of SOM that could be explained by higher exposure of the soil surface to the light, but this effect is not shown in the mineral layers, where the mineral soil from the stands under thinning present higher SOM content than those without, and higher degree of reduction of SOM in the deepest layers. This effect is not noticeable when λ data are averaged for all soil layers from one site (Fig. 6). The heat and CO_2 rates were both higher in the mineral soils under thinning than those of soils without this intervention.

The strength of λ as an indicator of SOM quality relays in being considered a potential index of SOM recalcitrance informing about the natural evolution of SOM, a subject under debate. Some reports argue a natural evolution of SOM towards a more oxidized state than the original one [32, 33], while others found the opposite trend, a natural evolution to a more reduced state [23, 34] in special when that evolution is tracked from the soil surface to soil deeper layers constituted by SOM at different degrees of decomposition. In these results, when the SOM nature based on their λ values is monitored following the depth gradient, in most of the cases SOM evolves to higher λ values than those on their surface (LF layer). The LF layer is usually less mineralized and rich in undegraded cellulose and lignin with Q_{SOM} values close to those reported for lignocellulosic material (about 18 kJ/g OM) [13, 35], that is more reduce than glucose (15.55 kJ/g OM) which are the values obtained in this work for eucalypt, and in a previous one, for oak and beech forests [15, 19]. Increased values for λ can be caused by the nature of the mineral soil, usually rich in polysaccharides, proteins and N–bearing compounds which increases with soil depth [3, 36, 37], as well as aliphatic microbial death biomass [29]. All of them are factors contributing to increase λ.

Nevertheless, comparison of SOM from young to mature forests show that the above reported natural SOM evolution could depend on additional external factors making that SOM can evolve to a more oxidized or to a more reduced state than the original one, which could explain the variability of arguments in the literature about that subject. Here, the progress of SOM to a higher degree of reduction from young to mature stands can be attached to SOM and C accumulation with time favoured by the preservation of the scrub. The evolution of SOM to a more reduced state with time is accompanied by depletion in the respiration rates that may contribute to C sequestration. C and SOM losses were the consequences of SOM evolution to a more oxidized state and higher respiration rates. The heat rate of soil microbial metabolism was less sensitive to the observed evolution of SOM. The nature of the substrates being metabolized given by the CR ratios followed the λ values when studied from young to adult forests but tend to decrease to more oxidized substrates than carbohydrates with soil depth, as observed in previous studies [38], or diminish due to changes in the microbial and metabolic structure with soil depth due to increased contribution of anaerobic metabolism [39]. Soil microorganisms use substrates more

oxidized, and therefore, with lower energy content than that of the entire SOM molecule, probably as a mechanism to preserve the energy and the C of SOM, in special in the mineral soil, where the C quantity depletes as SOM evolves with depth.

On the whole, application of these procedures enriches the information about the SOM evolution and, as shown in this paper, are sensitive to the different forest managements. Therefore, thermal analysis and calorimetry can help to develop the best strategies to keep forests and the forest soils.

Acknowledgements The authors thank Verónica Piñeiro and Montserrat Gómez of the RIAIDT analytical services, University of Santiago de Compostela, for calorimetric and DSC measurements. This research was funded by the Spanish Ministry of Science and Innovation Project PID2020-119204RB-C22 and through the Ramón y Cajal grant RYC2018-024939-I.

Author contributions All authors have contributed equally to the development of this work.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature. This work was funded by the Spanish Ministry of Science and Innovation Project PID2020-119204RB-C22 and Ramón y Cajal Grant RYC2018-024939-I.

Data availability The data sets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest There is not any competing interests dealing with this work.

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