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Effect of extreme temperatures on soil: A calorimetric approach

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ABSTRACT

The relation between soil organic matter dynamics and temperature is an important research topic, poorly understood yet. This study focuses on the effect of temperature on the heat rate of soil organic matter decomposition using different soil types, by simulating an extreme heat wave with a calorimeter. Heat rates were measured with an automated step-scan of temperature upward at 20, 30, 40, 50, and 60 °C, and downward at 40 and 20 °C to monitor how soil recovers after the heat wave. The results show enzyme-catalyzed bioprocesses are not the only reactions in soil mineralization. Other reactions can be distinguished from the shape of the curve of the heat rate versus temperature. These reactions coexist at normal environmental temperatures, and their relative contribution to soil organic matter mineralization rates varies with soil type.

1. Introduction

Soil constitutes, together with water, the most important primary resource on earth with direct impact on human food supply and on human survival. To preserve it has been a matter of concern in many scientific disciplines for centuries [1]. One of the most important subjects dealing with soil nowadays is the sensitivity of the soil system to temperature, due to the changing climate, to the trend of environmental temperatures to increase, and to the important role of soil organic matter (SOM) dynamics on the Earth's climate system, as a C source and a C sink [2].

The effect of temperature on SOM decomposition is commonly focused on soil microbiological reactions, using versions of the Arrhenius equation which predicts monotonic exponential increase in reaction rates with temperature [3]. Nevertheless, recent studies demonstrate the response of soil biodegradation to increasing temperature is not monotonic [4,5] limiting the viability of the Arrhenius model. For this reason, new alternatives are arising to explain the dependence of SOM dynamics to temperature when considered as an enzymatic system [6] but they are still poorly explored for applying to the soil. The existing previous work still determines the soil enzymatic rates for a short range of temperatures due to the long experimental soil incubations at lab conditions needed for that research. The minimum and maximum temperatures used are usually those involving enzymatic activity with very little information about the soil response to heat stress and practically no information about how soil recovers from extreme environmental temperatures.

Temperature is predicted to increase during this century and extreme values as high as 53.7 °C have been rated on Earth in 2017 [7]. Many places are being hit by increasing duration of extreme heat waves affecting agricultural lands. Therefore, models for predicting soil sensitivity to temperature should introduce knowledge about the evolution of the soil mineralization processes under extreme temperatures as well as, information about soil response to cooling. Calorimetry allows those measurements. New calorimeters register continuously the heat rate of a reaction under a changing temperature environment that can be designed to increase and to decrease along a broad range [8]. Recent applications show its sensitivity and relevance to detect heat rate changes with increasing temperature in soil samples [9,10] and it constitutes a still unexplored option to test models under extreme temperatures and when extreme temperature returns to lower values.

In this paper, a pioneer experiment using soils with different chemical, thermal and biological properties is designed to monitor changes in the heat rate from mineralization of SOM at temperatures from 20 to 60 °C and the soil response when cooling again to the initial temperatures. These data are used to test temperature dependent models for

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biomineralization and for direct SOM oxidation by atmospheric oxygen. Soil biomineralization is assumed in literature to be much more important than direct oxidation by oxygen at normal soil temperatures, but this assumption has not been tested for more extreme increasing temperatures in spite of recent works showing the role of abiotic processes in SOM mineralization [11].

2. Experimental

2.1. Theory

Soil biodegradation is mainly decomposition of dead plant lignocellulosic material made of hemicellulose, cellulose and lignin, by different enzymes linked to the soil microbial population [12] through well-known biochemical paths. Decomposition of cellulose and hemicellulose is mainly done by microbial action and direct chemical oxidation of cellulose products is unlikely to be significant. But in the case of lignin, direct oxidation occurs by insertion of O_2 molecules into secondary and tertiary C−H bonds to form hydroperoxides that can spontaneously react to product very reactive phenoxy and hydroxyl radicals. Oxygen also readily oxidizes polyhydroxyphenols to quinoids without CO_2 production [13]. Lignin can also be hydrolyzed by the exozyme secretome and by peroxidases produced by fungi. The oxygenated aromatic compounds produced by lignin hydrolysis and oxidation are poorly soluble, nor readily metabolized, and constitute the recalcitrant humates in aged SOM.

Therefore, SOM begins as macroscopic plant detritus that consists almost entirely of lignocellulose. The first step in bio-mineralization of SOM to CO_2 is colonization of these lignocellulose particles by microorganisms that secrete exozymes to catalyze lignocellulose hydrolysis into smaller molecules which are used by soil microorganisms as an energy and a C source for growing [14]. This activity controls the temperature response of bio-mineralization and can be chemically described by two equations:

$$\text{Lignocellulose} + H_2O = \text{saccharides} + \text{phenolics}\ \Delta_1 H \quad (1)$$

$$\text{Saccharides} + \text{phenolics} + O_2 = xCO_2 + yH_2O\ \Delta_2 H \quad (2)$$

The value of $\Delta_1 H$ is estimated from data on hydrolysis reactions of esters [15] where ΔH is typically small and can be endothermic or exothermic. $\Delta_2 H$ is Thornton's constant [16], −455 kJ/mol O_2. In soils, reaction (1) is catalyzed by exozymes and reaction (2) is catalyzed by oxidases inside active aerobic cells or by direct reaction of O_2 with SOM. Measuring the rate of reaction (1) is difficult since it requires measuring either the decrease of lignocellulose or the rate of production of some of the products in reaction (1) which are consumed by reaction (2). However, the overall rate can be measured as the rate of oxygen uptake, the rate of CO_2 production, or the heat rate from oxidation. The last can be easily measured by calorimetry where the rates of bio-mineralization and direct oxidation can be distinguished by the shape of the curve obtained by plotting the heat rates versus temperature. Biomineralization yields a bell shaped curve typical for biological systems. Direct oxidation will have a monotonic exponentially increasing curve.

The temperature dependence of direct oxidation is expected to follow an Arrhenius model:

$$RDO = Ae^{-Ea/kT} \quad (3)$$

where RDO is the rate of direct oxidation, A is a constant, Ea an activation energy, k is the Boltzmann's constant, and T is absolute temperature.

Biomineralization as a function of temperature can be described by a three state model [17]:

$$n_L \leftrightarrow n_A \leftrightarrow n_H \quad (4)$$

At a given temperature, n_L is the number of cold inactivated microorganisms and/or enzymes, n_A is the number of active microorganisms and/or enzymes, and n_H is the number of high temperature inactivated microorganisms and/or enzymes. Defining N as the total number of microorganisms and/or enzyme molecules, the fraction in the active state is n_A/N which is described as a function of temperature by:

$$RECO = (Cg_A e^{-\varepsilon/kT})/(1 + g_A e^{-\varepsilon/kT} + g_H e^{-\varepsilon'/kT}) \quad (5)$$

$RECO$ is the rate of enzyme catalyzed oxidation, C, g_A, g_H, ε and ε'are here considered as empirical fitting parameters. Relative activity, n_A/N, increases exponentially at low temperature, goes through a maximum as temperature increases, and then decreases at higher temperatures as expected for microbial activities [17,18].

The calorimetric measurements were designed according with the above theory defining temperature dependence of the bioenzymatic and direct oxidation reactions, with the goal of studying the soil response to extreme temperatures in a new way that could shed more light on this subject.

2.2. Material and methods

2.2.1. Soil samples

Soil samples with SOM of widely differing properties were selected in an attempt to link the observed oxidation rates to the chemical, thermal and biological properties of the samples. The main variables used to select soil samples were soil recalcitrance and different microbial structures, because of expected different sensitivities to temperature as a factor of these properties.

Cambisol [19], was collected at three different depths (0–10 cm, 10–20 cm and 20–30 cm) from pasture and pine forest lands in the northwest of the Iberian Peninsula (Spain, 43°37′51.94″N 7°37′22.63″) because SOM recalcitrance increases with depth. Sampling was done in paired plots under different management (pasture and forest) to determine the effect of differing soil uses. Samples of Leonardite (cat. #1BS104L) and Pahokee Peat (cat. #1R103H) obtained from the International Humic Substances Society [20] were included to compare soils with extreme different SOM properties.

2.2.2. Elemental and thermal properties

Elemental composition of the Cambisol samples was determined with a LECO elemental analyzer. Elemental data for Pahokee peat and Leonardite data were obtained from the International Humic Substances Society [20].

Thermal stability of the soils was studied by thermogravimetry (TG) (TGA-DSC1 Mettler Toledo) by well-known procedures [21]. SOM Thermal properties were established based on T50-DSC and T50-TG values [22,23], heat from SOM combustion, Q_{SOM}, SOM percentage and char percentage.

2.2.3. Microbiological properties

Microbial analysis of the samples was done by ARISA using Power Soil TM DNA Isolation Kit (MO BIO Laboratories, California, USA) according to manufacturer's specification and common protocols [24,25] to provide bacteria and fungi OTUs. The complete procedure is specified in detail as supplementary material.

2.2.4. Calorimetric heat rate measurements

Soil samples collected for calorimetric measurements were sieved (< 0.5 mm) and stored inside polyethylene bags for one month at 4 °C and at 45% of their water holding capacity (WHC). Just before these measurements, 10 g of each of the soil samples were first equilibrated at the initial temperature of the calorimetric measurements (20 °C). After this equilibration, samples were brought to 60% of WHC and stabilized after rewetting for 4–8 days, depending on the soil sample, at 20 °C inside polyethylene bags. Once samples are stable after rewetting, 0.8 g aliquots were introduced into 4 ml stainless steel ampoules which were

then sealed and inserted into a calorimeter (TAM III, TA instruments, Lindon, UT) with six channels. Heat rates (φ = dQ/dt) were measured with a step-scan of isothermal temperatures designed to measure the response of soil to both increasing and decreasing temperatures. Increasing temperatures at 20, 30, 40, 50 and 60 °C tested the response of the soil heat rates to increasing extreme temperatures and decreasing from 60 °C to 40 °C and then to 20 °C tested the ability of the soil samples to recover from the high temperatures. The duration of each of the isothermal periods was about 15 h, extending the duration of the last measurement at 20 °C after the heat wave to about 48 h. The increase of temperature between isothermal periods was at 0.042 °C/min and took about 4 h. Cooling took 4 h at 0.083 °C/min. The whole measurement was done along one week with the same soil samples. To ensure the oxygen in the ampoules was not depleted and to avoid CO_2 accumulation inside ampoules during the measurement, samples were taken out of the calorimeter and opened twice during the week of measurement: during the scan from 40 to 50 °C and from 40 to 20 °C. Samples were re-inserted into the calorimeter 30 min before the new isothermal period started, after incubation during the temperature scan period in an oven at the temperature of the next calorimetric measurement. The identical scan procedure was applied with empty ampoules to determine blank heat rate values to subtract from heat rate measurements on the soil samples, following recommendations in previous papers [26]. The calorimeter continuously records the heat rate in microwatts (φ = dQ/dt) in a result file that can be plotted versus time (φ-t plots). The quantitative heat rate for each temperature is determined by integrating the φ-t plots at each isothermal period over a time interval of 10 h to give the heat rate (*Rq*) in milijoules per gram of soil and hour (mJ/g h).

2.2.5. Statistical analysis

The significance of differences among heat rates in the different soils was tested by one way ANOVA by considering the heat rate at different temperatures from each soil type as levels of the studied factor ($n = 14$, $p < 0.05$). Normality and homogeneity of variances of the data were evaluated by the Shapiro-Wilk and Levene tests respectively. Conversion to logarithms was applied when necessary. Comparison of temperatures after the heat stress at 60 °C with the initial ones was done by a paired samples *t*-test. Pearson's correlations were determined to study the effect of the elemental, thermal and microbiological soil properties on the observed sensitivity to temperature of samples. All data are presented on an average basis (n = 2 or 3 ± SD). Sample-by-binned-OTU tables for bacteria and fungi were analyzed separately and used to perform a hierarchical clustering to create a dendrogram based on unweighted pair-group average (UPGMA) and constrained Bray Curtis similarity index using Past 3.14. Diversity indices for bacteria and fungi were also determined (Shannon, Simpson and Evenness).

3. Results and discussion

3.1. Soil elemental, thermal and microbiological properties

Peat and Leonardite are the samples with the highest carbon, C, and SOM percentages (Table 1). In cambisol samples, C and SOM percentages were higher in the pine forest than in the pasture. Both C and SOM decrease with soil depth. C/N ratio varies from 55 to 13 among samples.

Thermal stability of samples as measured by the T50-DSC and T50-TG (Table 2) followed the order Leonardite > Peat > Cambisol. Cambisol samples show no remarkable differences in thermal stability under pasture or forest or with depth. Q_{SOM} values (Table 2) tend to be higher in Peat and Leonardite than in cambisol samples and all samples show higher Q_{SOM} values than for carbohydrates (15.55 kJ/g OM) and lignocellulosic material [27] (18 kJ/g OM) showing SOM at a similar degree of reduction as reported for lignin material [27,28]. Leonardite and Peat have the smallest char percentages after combustion. Thermal stability is proposed as an index of SOM recalcitrance [22,23] and here it is used to link the soil sensitivity to temperature with the SOM properties.

ARISA yields bacterial and fungi OTUs falling into 7 different clusters (cut-off at 0.4 similarity index). Dendrograms are shown as supplementary material (Figs. S1 and S2). The only samples clustering at 40% similarity are samples from the pasture 10–20 and 20–30 cm soil depths. Therefore, most of the samples differ in their microbiological

Table 1
Elemental composition of the samples.

Samples	C (%)	OM (%)	N (%)	C/N
Pine 0–10 cm	8.2 ± 0.2	20 ± 2	0.34 ± 0.02	24
Pine 10–20 cm	5.1 ± 0.4	12 ± 1	0.26 ± 0.01	20
Pine 20–30 cm	2 ± 0.1	5.0 ± 0.2	0.16 ± 0.01	13
Pasture 0–10 cm	5.7 ± 0.5	10.5 ± 0.5	0.45 ± 0.02	13
Pasture 10–20 cm	4.3 ± 0.1	8.8 ± 0.5	0.25 ± 0.01	17
Pasture 20–30 cm	1.7 ± 0.1	4.6 ± 0.2	0.13 ± 0.01	13
Peat	45.7 ± 1	83 ± 1	3.13 ± 0.2	15
Leo[a]	49.2 ± 0.4	84 ± 2	0.9 ± 0.05	55

[a] Leo is the sample of Leonardite.

Table 2
Thermal properties of the soil samples.

Samples	Char (%)	Q_{SOM} kJ/gOM	T50-TG (°C)	T50-DSC (°C)
Pine 0–10 cm	78 ± 2	22 ± 3	343 ± 1	344 ± 3
Pine 10–20 cm	89 ± 1	24 ± 4	358 ± 3	336 ± 2
Pine 20–30 cm	95 ± 3	23 ± 2	352 ± 1	313 ± 2
Pasture 0–10 cm	89 ± 3	21 ± 3	338 ± 3	337 ± 3
Pasture 10–20 cm	91 ± 1	26 ± 4	354 ± 3	344 ± 2
Pasture 20–30 cm	92 ± 3	23 ± 2	357 ± 3	344 ± 3
Peat	18 ± 2	25 ± 2	391 ± 3	394 ± 3
Leo[a]	17 ± 1	26 ± 1	414 ± 0.1	408 ± 2

[a] Leo is the sample of Leonardite.

Table 3
Bacterial diversity of soils. Taxa_S is the number of taxa present in the samples. Simpson, Shannon and Evenness are diversity indices.

Samples	Taxa_S	Simpson (1-D)	Shannon_H	Evenness E^H/S
Pine 0–10 cm	6	0.794	1.67	0.881
Pine 10–20 cm	17	0.901	2.51	0.721
Pine 20–30 cm	34	0.964	3.41	0.891
Pasture 0–10 cm	28	0.942	3.07	0.770
Pasture 10–20 cm	31	0.958	3.28	0.858
Pasture 20–30 cm	32	0.949	3.21	0.771
Peat	8	0.835	1.93	0.860
Leo[a]	7	0.848	1.92	0.970

[a] Leo is the sample of Leonardite.

Table 4
Fungal diversity of soils. Taxa_S is the number of taxa present in the samples. Simpson, Shannon and Evenness are diversity indices.

Samples	Taxa_S	Simpson (1-D)	Shannon_H	Evennes E^H/S
Pine 0–10 cm	25	0.928	2.90	0.726
Pine 10–20 cm	6	0.795	1.69	0.903
Pine 20–30 cm	25	0.903	2.62	0.548
Pasture 0–10 cm	11	0.873	2.20	0.820
Pasture 10–20 cm	21	0.900	2.48	0.570
Pasture 20–30 cm	22	0.922	2.75	0.709
Peat	15	0.838	2.19	0.597
Leo[a]	21	0.733	2.07	0.379

[a] Leo is the sample of Leonardite.

properties and in the case of cambisol, different management (forest and pasture) yielded differing microbial structures in the uppermost samples (0–10 cm). Cambisol samples from the upper horizons in the pasture showed the highest bacterial diversity (Simpson 1-D, Shannon and Evenness) (Table 3). Fungal diversity (Table 4) followed the order Pine 0–10 cm > pasture 0–10 cm > Peat > Leonardite. Fungal diversity tends to decrease with higher SOM thermal stability while bacterial diversity is more insensitive to the thermal stability in the upper horizons. Fungal diversity increases with soil depth in the cambisol under pasture while bacterial diversity increases with depth in the pine forest.

Pearson's correlations show the links among these elemental, thermal and microbiological properties for all the samples (n = 8). C content positively correlates with T50-TG ($r^2 = 0.92$; $p < 0.001$), T50-DSC ($r^2 = 0.95$; $p < 0.0001$) and with the bacterial OTUs ($r^2 = -0.72$; $p < 0.05$). C/N ratio correlates with T50-TG ($r^2 = 0.73$; $p < 0.05$) and with the Simpson index for fungi ($r^2 = -0.74$; $p < 0.05$). Therefore, increased C content favors thermal stability in these samples and decreases bacterial diversity, while higher C/N ratios deplete fungal diversity. The char percentage (Table 2) is higher in the cambisol samples than in peat and Leonardite and increased with soil depth in both forest and pasture.

Char content is positively correlated with the bacterial OTUs ($r^2 = 0.72$; $p < 0.05$) and with the Shannon diversity index for bacteria ($r^2 = 0.75$; $p < 0.05$) but it is unclear why because the role of char on soil elemental and biological properties is still poorly explored [29]. These results suggest that the char derived by TG analysis could be related with the degree of soil mineralization, which is the product of equations (1) and (2), and that increased degree of soil mineralization favors bacterial diversity more than fungi.

3.2. Calorimetric results

Changes of the soil decomposition rate, measured in microwatts, φ, with temperature can be observed in Fig. 1. All samples show a fast response to the change of temperature as found in previous papers [9,10]. φ is constant with time at 20 and 30 °C in most of the samples, with the exception of peat that shows unstable decomposition rates. From 40 °C to 60 °C, φ is unstable in most of the samples, with increasing or decreasing rates depending on the soils, suggesting a change in the nature of the reactions taking place at that temperature range.

The temporal decay of the rates during the isothermal measurements with increasing temperature has been attached to the fact that enzyme activity decreases at extreme temperatures [30]. In general, Fig. 1 clearly shows that evolution of φ with temperature is different for each soil. It can also be observed that φ values are zero after the heat wave in the cambisol samples from 10 to 20 and 20 to 30 cm, while peat, Leonardite and cambisols from 0 to 10 cm have remaining activity after the heat wave. It is observed in Fig. 1 as well, that φ at each temperature decreases with soil depth in cambisols.

The fact that φ values are not constant during the isothermal phase of the measurement makes necessary to integrate the isothermal phases to obtain an average of the heat rates, *Rq*, in millijoules per gram of soil and hour (mJ/g h). These rates for each of the temperatures are the ones represented in Figs. 2 and 3 by the red lines during the heating from 20 to 60 °C (Table S3 in supporting material) ANOVA indicated

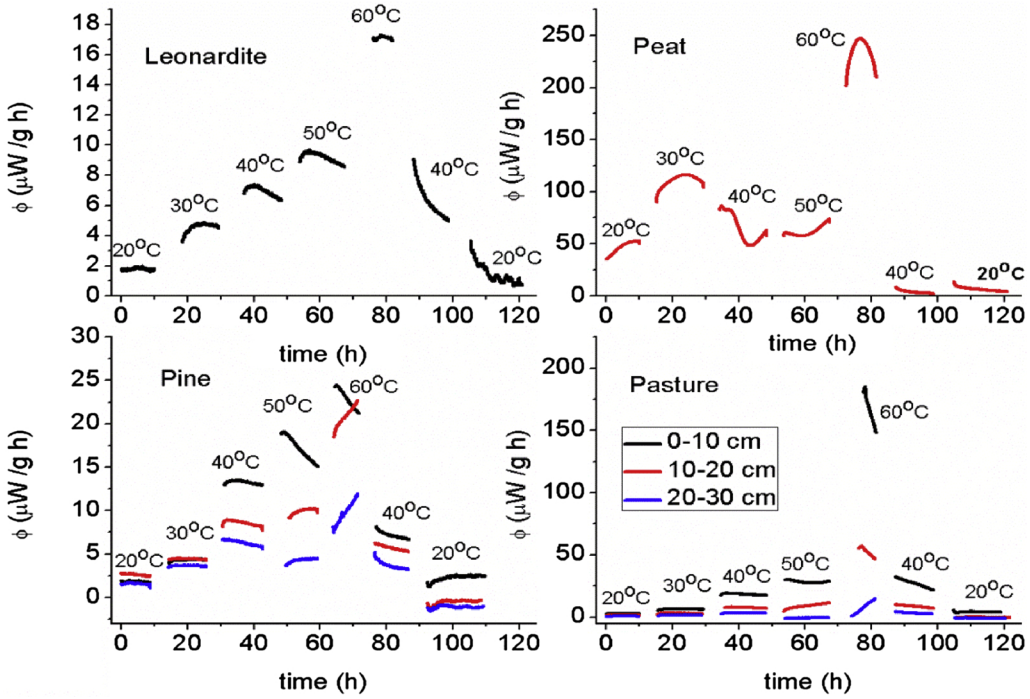

Fig. 1. φ-t plots representing the evolution of the soil decomposition rates with temperature.

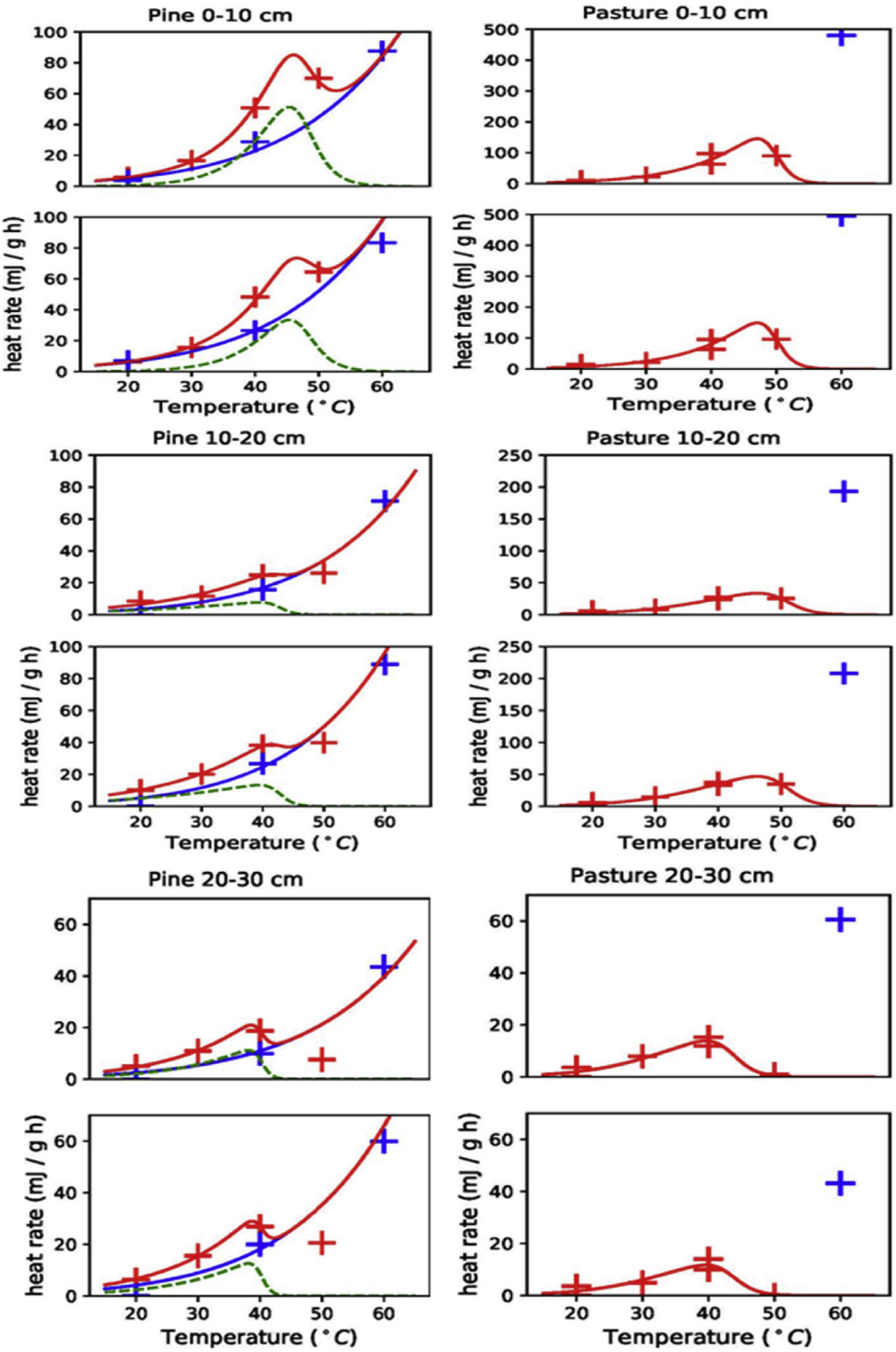

Fig. 2. Averaged heat rates, *Rq* (red lines), fit to the models given in Eqs. 3 (solid blue line) and 5 (dashed green lines) of all the cambisol samples under pine and pasture, showing the evolution of these data with soil depth (duplicates) (For interpretation of the references to colour in this figure legend and text, the reader is referred to the web version of this article).

evolution of these heat rate values are significantly different among samples from the soil surface (levels = 4, n = 56, $p < 6.5 \times 10^{-4}$). Comparison of cambisol samples from different depths (levels = 6) yielded significant differences too (n = 84, $p < 9 \times 10^{-3}$). Thus, dissimilarities in SOM nature and soil microbial population yield different sensitivity to heat stress.

Red lines in Figs. 2 and 3 exhibit an easily recognizable change of the heat rate increasing trend with temperature in samples, with maximum heat rate values between 30 and almost 50 °C during the upward scan, followed by a variable evolution of the heat rate with the temperature increase, reinforcing the existence of other reactions taking place in soil at extreme temperatures, that could be direct oxidation as proposed here, but also activation of thermophiles in some of the samples. The *t*-test showed rates at 40 and 20 °C after the heat wave were significantly lower than the initial ones ($p < 0.05$) in peat, Leonardite and pine samples, but not in the pasture samples (Fig. 4). Lower rates at 40 °C after the heat stress, is interpreted here as a loss of enzymatic microbial activity.

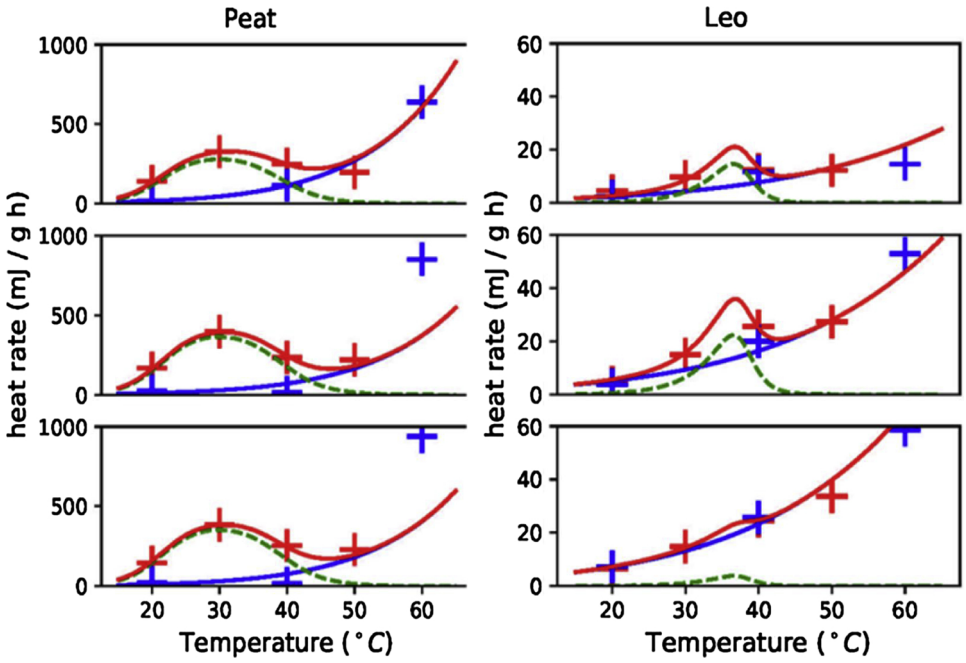

Fig. 3. Averaged heat rates, *Rq*, (red lines) fit to the models given in Eqs. 3 (solid blue line) and 5 (dashed green lines) for all Peat and Leonardite samples (triplicates) (For interpretation of the references to colour in this figure legend and text, the reader is referred to the web version of this article).

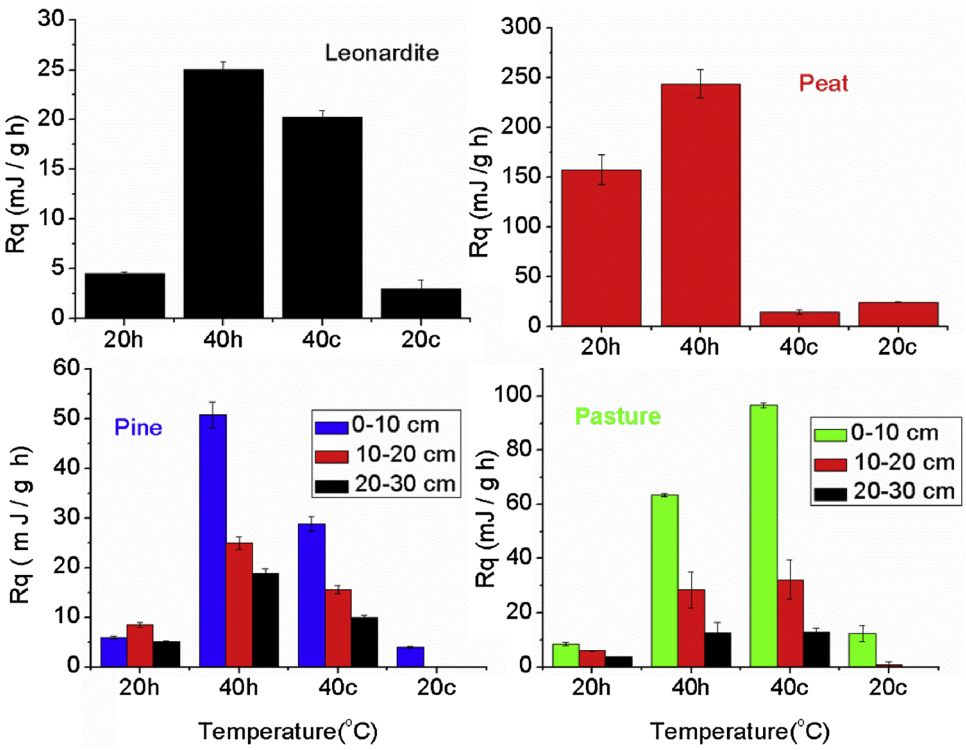

Fig. 4. Comparison of heat rate values *(Rq)* during heating (20 h and 40 h) and cooling (20 c and 40 c).

Figs. 2 and 3 also shows curves obtained by fitting averaged heat rates, *Rq*, to the models for direct oxidation (blue lines) and for enzyme catalyzed oxidation (green lines) in Eqs. 3 and 5 respectively. Where the second measurements of *Rq* at 40 and 20 °C during the down scan, were significantly lower than the first measurements, *Rq* at 60, 40 and 20 °C were assumed to be due to direct oxidation, and these data were fit to Eq. 3. These results were then subtracted from the first measurements at 20, 30, 40 and 50 °C during the up scan and the remainder fit to Eq. 5. In the cambisol pasture samples, *Rq* values when cooling, were not significantly different from the first ones when heating, so data from 20 °C to 50 °C were fit to Eqs. 5 and 3 for direct oxidation was not applied.

These fitting parameters are given in Table S4 as supplementary material. Figs. 2 and 3 show the evolution with temperature of all these data, where it can be observed that bio-mineralization (green lines) and direct oxidation (blue lines) may occur concurrently, and how contribution of direct oxidation is higher as temperature increases. It can be observed as well, how direct oxidation with respect to enzyme-

Table 5
Characteristics of oxidation reactions in the samples.

Samples	T_{max}[a] (°C)	Normalized rate[b] at T_{max}	Activation energy[c]/eV
Pine 0–10 cm	45.4	0.177	0.58
Pine 10–20 cm	39.3	0.042	0.61
Pine 20–30 cm	38.1	0.024	0.58
Pasture 0–10 cm	47.1	0.021	ND
Pasture 10–20 cm	46.2	0.561	ND
Pasture 20–30 cm	39.6	0.533	ND
Peat	30.0	0.090	0.75
Leo[d]	36.6	0.054	4.65

Note that 0.60 eV is equivalent to 58 kJ/mole or Q10 = 2.2.
[a] Temperature of maximum rate of enzyme-catalyzed reaction.
[b] Rate of the enzyme-catalyzed oxidation as the fraction of total activity expressed as T_{max}.
[c] Activation energy of direct oxidation of SOM by atmospheric oxygen.
[d] Leo is the sample of Leonardite.

catalyzed oxidation would vary with SOM type. The peat SOM shows little, if any, direct oxidation below 50 °C (Fig. 3) while the rest of the samples present varying contributions of direct oxidation relative to enzymatic activity. Relative susceptibility to direct oxidation at 60 °C can be assessed from the rates measured at that temperature: peat > pine > Leo in samples from the soil surface. It can be observed in Fig. 2 that in cambisol pine samples, relative susceptibility to direct oxidation decreases with soil depth (blue lines). Therefore, labile samples probably have higher amounts of lignin at lower degree of degradation which would be more susceptible to direct oxidation as temperature increases than recalcitrant samples with more humifed organic matter.

A recent publication evidences too that soil mineralization takes place by two processes as assumed here: abiotic conversion of non-bioavailable forms into available forms (the Regulatory Gate) and biological mineralization [11]. These findings have serious implications for theories involving the effect of climate change.

Only the N content of the samples correlated positively ($r^2 = 0.97$; $p < 0.0001$) with the heat rates at 20, 30 and 40 °C as expected for bio-mineralization. Figs. 2 and 3 also yield the temperatures at which maximum heat rates are obtained by bio-mineralization (green lines) before beginning to decline as temperature increases. Those temperatures are shown in Table 5. They correlate with the N content and T50-TG values of the samples ($r^2 = -0.73$, $p < 0.05$; $r^2 = -0.74$, $p < 0.05$ respectively) indicating that lower soil thermal stability increases the maximum temperature at which soils are capable of maintaining their enzymatic activity, before enzymes start to be deactivated or denatured. No correlation was found between the rates and the microbial properties reported here, which is not surprising because the microbial structure is not necessarily linked to bio-mineralization since different microorganisms can do the same metabolic functions [31].

These results suggest that soil sensitivity to temperature and the relation with soil properties cannot be defined by the biodegradation rates alone, but together with temperatures at which maximum biodegradation rates are reached before beginning to decline as temperature increases further. More authors [4,5,17] have recently reported maximum temperatures linked to soil enzymatic activity ranging between 30 and 40 °C as obtained here. These temperatures tend to decrease with soil depth and the correlation found with the T50-TG suggests that higher SOM recalcitrance could be associated with higher sensitivity to temperature, in agreement with the carbon-quality-temperature-hypothesis [32], when those temperatures are used as the indicator. The model suggested in this paper also evidences that soil could be directly oxidized and that more labile SOM could be more sensitive to direct oxidation than recalcitrant SOM, due to higher undegraded lignin content. Thus, the reason for the lack of agreement involving the carbon-quality-temperature hypothesis could be that most of the previous work does not consider that mineralization rates do not increase monotonically, as well as the role of abiotic processes on soil sensitivity to temperature, such as the direct SOM oxidation as part of the Regulatory Gate [11].

The microbial population in cambisol pasture soils was the only one not affected by exposure to 60 °C as shown by the recovered microbial activity after cooling to the lower temperatures (Figs. 1 and 4), suggesting higher resistance to temperature in this soil ecosystem. The explanation can be attached to the denaturation temperatures of exoenzymes produced by soil microbes. Incubations of soil under heat stress conditions have been shown to rapidly reduce or completely inhibit β-glucosidase, α-1,4-glucosidase, cellobiohydrolase, *N*-acetyl-glucosaminidase, phosphatase and sulfatase enzymatic activities [33,34]. Literature also shows that xylanase, which is produced by both bacteria and fungi, has an optimum activity at 40–60 °C and is very thermally stable [35,36]. Since grasses produces xylan as a major component of lignocellulose, this could explain the higher resistance to 60 °C in the pasture cambisol samples seen here. It may also explain literature reporting dissimilar sensitivities to temperature at different soil depths [37,38].

All these features support the role of calorimetry to improve knowledge about the effect of temperature on soil chemistry and biochemistry, and reinforce the need to improve current models assessing soil sensitivity to temperature. The models tested here are an additional option to explore, that would increase accuracy in forecasting the response of SOM to climate change, and these results, a proof of concept that SOM sensitivity to temperature may be ruled by additional indices and reactions that are not considered by the previous existing models published by the literature.

4. Conclusions

SOM sensitivity to temperature is not exclusively determined by the soil enzymatic activity.

Bio-enzymatic activity increases with temperature only up 30–50 °C depending on soils. Samples with lower thermal stability support higher temperatures limiting the bio-enzymatic reactions.

The contribution of direct oxidation of SOM would increase with increasing temperature.

Increased recalcitrance makes SOM bio-enzymatic microbial activity more sensitive to temperature while labile SOM could be more sensitive to direct oxidation.

Declaration of interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.tca.2018.10.010.

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