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Chemical and microbial activation energies of soil organic matter decomposition

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Abstract Present concepts emphasize that substrate quality exerts an important control over substrate decomposability and temperature sensitivity of heterotrophic soil respiration (Rh). In this context, soil organic matter (SOM) quality is defined by its molecular and structural complexity and determines the ease by which substrate is oxidized. However, temperature not only affects SOM oxidation rates but also equally the physiology of soil microorganisms, making it difficult to use respiration rates as indicative for the quality inherent to a substrate. One way to distinguish these two would be to measure organic matter oxidation by controlled combustion and to compare the temperature sensitivity of this chemical process to that of enzyme-catalyzed microbial respiration. We analyzed reaction rates, thermal stability indices, and activation energies (Ea) during (i) microbial respiration (Ea_{Rh}) and (ii) controlled combustion by differential scanning calorimetry (DSC) (Ea_{DSC}) of the same set of mineral and organic soils. A high thermal stability coincided with small heterotrophic respiration rates, indicating that thermal stability may be useful as a proxy for biological degradability. Under ambient conditions, enzymes greatly reduced Ea on average from 136 (Ea_{DSC}) to 87 (Ea_{Rh}) kJ mol^{-1}, thereby increasing CO_2 release by a factor of 1.5 * 10^7 relative to the noncatalyzed chemical reaction. However, temperature dependency of chemical and microbial oxidation was not correlated, suggesting that they are determined by different sample properties. A high temperature sensitivity of microbial respiration is linked to parameters independent of chemical oxidizability, in our case, organic matter C/N ratio and soil pH. These factors are important controls for microbial, but not for chemical, oxidation.

Keywords Activation energy · Organic soil · Respiration · pH · Calorimetry

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Introduction

In many chemical or microbial processes, a dependency of the reaction rate *k* on temperature is observed. Such a dependency is often satisfactorily described by Arrhenius kinetics, for which *k* is a function of temperature, activation energy (Ea), and a pre-exponential factor that quantifies the theoretical rate in the absence of the activation energy. Davidson and Janssens (2006) argued that the inherent molecular structure and complexity of organic compounds undergoing decomposition in soil controls their activation energy in a direct way, which they referred to as the intrinsic temperature sensitivity of decomposition. High intrinsic temperature sensitivity may be positively related to the number of enzymatic steps required for substrate breakdown, and the latter has been suggested to define substrate quality (Bosatta and Ågren 1999). Substrate quality, thus, refers to the chemistry and molecular complexity of the substrate. The hypothesized higher temperature sensitivity of a poor quality substrate, as developed by Bosatta and Ågren (1999), has been interchangeably referred to as 'temperature-quality-hypothesis' (Wetterstedt et al. 2010) or 'carbon-quality-temperature (CQT) theory' (Kleber 2010). In organic soils, substrate quality is closely associated with organic matter (OM) chemistry and molecular size, whereas in mineral soils, desorption, e.g., from Fe, Al, and Mn oxides or phyllosilicates, and cleavage of linkages between OM surfaces and metal ions require additional energies that must be overcome for decomposition (von Lützow and Kögel-Knabner 2009).

Substrate quality, as defined here, is linked to the biochemical functioning of soil organic matter as a source of energy for microbial metabolism. Although there is theoretical (Ågren and Bosatta 2002) and experimental (e.g., Fierer et al. 2005; Waldrop and Firestone 2004; Conant et al. 2008; Craine et al. 2010a) evidence for a recalcitrance effect on the temperature sensitivity, intrinsic recalcitrant properties are difficult to capture because different processes in C destabilization and their temperature sensitivity act in concert with effects of temperature on the physiology of the soil microflora. These two mechanisms are difficult to separate experimentally (Conant et al. 2011).

Enzyme catalyze microbial reactions such as polymer breakdown by reducing Ea for a given reaction and, thus, increase k by several orders of magnitude compared to the noncatalyzed reaction (Nelson and Cox 2008). Therefore, a comparison between the noncatalyzed reaction, hereinafter referred to as 'chemical oxidation,' and the resistance to enzyme-mediated oxidative decay, hereinafter referred to as 'microbial oxidation,' could provide insight into the intrinsic temperature sensitivity of OM oxidation. Controlled burning experiments revealed empirical relationships between thermal and chemical (Lopez-Capel et al. 2008) or microbial (Grisi et al. 1998; Harvey et al. 2012) characteristics of soil organic matter (SOM) or other organic compounds. These linkages between thermal stability indices and OM decomposability prompt a discussion directed towards possible thermal proxies for biogeochemical stability of SOM (Plante et al. 2009). However, control of thermal stabilities by the degree of decomposition can be complex (Rovira et al. 2008) and it has proven difficult, so far, to find a mechanistic understanding needed for a substantiated evaluation of thermal indices.

Thermal stability is indicated by the susceptibility to chemical oxidation at a particular temperature, and the size and position of the exothermic peaks. It not only depends on the substrate's chemical characteristics but also on its degree of polymerization and, thus, the molecular structure, the degree of mineral association, and the spatial arrangement of molecules and macrostructures (Leifeld 2008; Leinweber and Schulten 1999; Plante et al. 2009; Vander Wal and Tomasek 2003). Microbial decomposition rates also depend on these characteristics. Burning experiments may, thus, provide an affordable, rapid, and information-rich chemical method to detect meaningful patterns in SOM decomposability. Moreover, controlled burning at different heating rates also allows measurement of the Ea for the oxidation reaction (ASTM 2005) and, thus, a direct estimation of the intrinsic temperature sensitivity of chemical oxidation with respect to substrate properties such as carbon speciation, degree of polymerization, and presence of soil minerals.

So far, there has been no attempt to relate Ea measured from chemical oxidation in such a way to any microbial index of SOM quality or temperature sensitivity. In this work, a range of mineral and organic soils was subjected to controlled chemical oxidation in a differential scanning calorimeter (DSC), and activation energies of the chemical process (Ea_{DSC}) were measured and compared to the temperature sensitivity of heterotrophic respiration (Rh) of the same set of samples (Ea_{Rh}). We hypothesize that (i) Ea_{Rh} must be significantly lower than Ea_{DSC} due to the catalyzing effect of enzymes, (ii) Ea_{DSC} gives insight into inherent molecular and structural substrate properties, and (iii) Ea_{Rh} should be higher for mineral soils due to the necessary desorption prior to substrate uptake. We also studied possible relationships between Ea_{Rh} and DSC parameters that could be used as a proxy for the stability of SOM against microbial oxidation and thus as a quick and inexpensive means of assessing SOM quality in reference to decomposability and turnover.

Material and methods

Soil samples were collected from depths between 0 and 36 cm as intact 100-cm^3 cores (height: 4.1 cm, diameter: 5.6 cm) from two grassland sites in Switzerland: Seebodenalp (SA, n=11) and Alp Flix (AF, n=8). Site SA comprises histosols (fens and bogs) with SOC contents of between 17 and 53 % and pH ($CaCl_2$) values between 3.1 and 5.1. SA is located at around 1,050 masl with a mean annual temperature (MAT) of 7.3 °C and a mean annual precipitation (MAP) of 1,330 mm. It is mown once per year. AF is a subalpine site at around 2,000 masl, MAT 2.8 °C, MAP 1,050 mm, consisting of both a pasture and a meadow field on mineral soil (organic carbon (OC) 5.1–7.3 %; pH 4.5 to 5.4)). Site details of SA and AF are given in Rogiers et al. (2008) and Leifeld and Fuhrer (2009), respectively, and a summary of important soil properties is listed in Table 1. Both sites are only moderately managed and are not fertilized. Alp Flix receives small amounts of manure from cattle (summer grazing or haying with stocking density of about 0.2 livestock units), but no external inputs.

Laboratory incubations of soil samples and calculation of respiration temperature sensitivity

During the vegetation period at both sites, diurnal soil temperature amplitudes are typically around 10 °C leading to daily minima of c. 15 °C and maxima of c. 25 °C, and this temperature range was chosen for the incubation temperatures in the laboratory. At both sites, we sampled soils using intact cores to include factors such as mobilization, transport, and transfer of carbon compounds in soil that may, if ignored, bias temperature effects, as discussed in Mahecha et al. (2010). By measuring the temperature sensitivity in short-term laboratory incubations with short-term temperature manipulations, we can rule out a decline in substrate availability as a confounding factor in the

Table 1 Overview of physico-chemical properties and logarithmic respiration rates (ln k Rh) of the studied soils

Soil sample	SOC (mg g^{-1} soil)	C/N	pH	ln k Rh at 25 °C (μg CO_2-C g^{-1} OC day^{-1})	Ea_{Rh} (kJ mol^{-1})
$SA1_{a2}$	415.2	15.2	4.1	6.77	93.6
$SA2_{b2}$	469.8	18.7	4.1	6.38	84.2
$SA3_{b34}$	525.8	38.8	3.1	5.98	119.9
$SA4_{c2}$	482.1	23.0	3.9	6.93	95.1
$SA5_{d2}$	335.1	16.0	4.2	7.10	84.1
$SA6_{d22}$	490.6	27.7	3.9	5.58	117.9
$SA7_{e2}$	348.9	16.8	4.2	7.83	98.7
$SA8_{f2}$	324.4	16.1	5.1	7.82	85.4
$SA9_{g2}$	213.0	12.3	4.8	7.73	83.1
$SA10_{h2}$	172.8	11.4	4.7	8.22	85.1
$SA11_{j2}$	183.9	13.3	4.9	8.15	80.7
$AF1_{a2}$	58.7	11.1	5.4	7.32	75.4
$AF2_{a6}$	71.2	11.3	4.5	7.64	67.3
$AF3_{b2}$	57.0	10.9	5.2	7.04	84.8
$AF4_{b6}$	68.2	11.0	4.5	7.38	76.9
$AF5_{c2}$	50.7	11.6	4.8	7.52	78.6
$AF6_{c6}$	51.9	12.4	5.0	7.55	77.5
$AF7_{d2}$	72.6	11.3	4.7	7.22	79.8
$AF8_{d6}$	63.7	11.7	5.0	7.19	78.7

Letter denotes subplot at site SA or AF; number denotes mean sampling depth (cm)

study of temperature/quality relationships (Wetterstedt et al. 2010). Furthermore, we can exclude thermal adaptation of microbial communities (Balser and Wixon 2009) or the formation of adapted isoenzymes with respect to different environmental conditions (Bradford et al. 2008). Both effects are unlikely to play an important role in short-term temperature variations over the 1–2 days or so that we used to mimic in situ diurnal variations at our sites. The heterotrophic respiration rate (Rh) of intact soil cores was measured over periods of 2–24 h, depending on sample activity with an infrared sensor (measuring range 0–3 % vol.) in a temperature-controlled incubation chamber at 25 °C (Rh_{25}) and 15 °C (Rh_{15}) after the cores had been adjusted over a period of 7 days to a water tension of 100 hPa. CO_2 concentrations increased linearly over the selected measurement periods. Simultaneous oxygen measurements in the headspace were used as an additional control to prevent O_2 deficiency and were not allowed to drop below 19 % vol. The Rh was corrected for dissolved CO_2. Aqueous concentrations are inferred from measured pCO_2 in the chamber headspace using Henry's law and pH- and temperature-dependent dissociation constants for HCO_3^- and CO_3^{2-}, assuming an instantaneous thermodynamic equilibrium. Total change in CO_2 storage was, thus, computed considering measured gaseous CO_2 contained in the headspace and of dissolved inorganic carbon. It is given as ln micrograms C per gram OC per day (Table 1). The temperature sensitivity of Rh of each sample was expressed as the activation energy Ea [joules per mole] using the conventional Arrhenius equation:

$$Ea = -R \times T \times \ln\left(\frac{k}{A}\right) \quad (1)$$

where R is the gas constant, T is the absolute temperature, k is the respiration rate, and A is the frequency or pre-exponential factor. The slope of ln k vs. T^{-1} equals $-Ea / R$.

After incubation, samples were sieved to <2 mm, dried at 105 °C, and ground. Soil C and N was determined by elemental analysis (Euro EA, HEKAtech, Germany) and soil pH was measured in the supernatant of a 0.01-M $CaCl_2$ solution.

Thermal analysis and chemical activation energy of soil samples

Thermal stability of dried and milled samples was measured during controlled combustion in a differential scanning calorimeter (DSC Q100, Waters, USA). To avoid possible charring or peak shifts during combustion (Leifeld 2007), samples were diluted with Al_2O_3 to obtain a C concentration of 3 %. Samples were heated in synthetic air (50 ml min^{-1}) from room temperature to 600 °C with a heating rate β of 5, 12.5, and 20 °C min^{-1}, and their differential heat flux Φ [watts per gram] was recorded. The measured thermal stability parameters were temperature and heat flux at peak temperature of the first main exotherm, as well as the 50 % burnoff temperature (temperature at which 50 % of the total heat of reaction has evolved, degrees Celsius; hereafter referred to as T50). The first major exothermic peak, appearing at lower temperatures, is attributed to

easily decomposable OM, as indicated by composting studies (Dell'Abate et al. 2000; Leifeld 2008), and is, thus, more meaningful for any comparison with short-term microbial reaction rates compared to the overall burning pattern of the sample, which also includes thermally stable compounds such as pyrogenic carbon (Leifeld 2007; Plante et al. 2009).

From the DSC measurements at three different heating rates (see above), Arrhenius parameters of the chemical oxidation were calculated according to ASTM (2005). This is based on the principle of a shift in peak temperatures with a change in heating rate. Briefly, Ea [joules per mole] is a function of β [Kelvin per minute] and the absolute peak temperature T:

$$Ea_{DSC} = R \times \frac{d\left(-\ln\beta \Big/ T^2\right)}{d\left(1/T\right)} \quad (2)$$

where R is the gas constant. Activation energies were calculated according to Eq. 2 and were later used to compute hypothetical energy and, thus, CO_2 fluxes upon chemical oxidation at 25 °C (k_{DSC25}) as described above. Hence, Eq. 2 provides a measure of the activation energy of the chemical process (Ea_{DSC}) that is directly comparable to the activation energies measured for microbial decomposition (Ea_{Rh}).

A peak heat flux at a rate of 1 °C min^{-1} was calculated based on the relationship between Φ and the peak temperature (R^2>0.99). This was done to avoid unnecessarily long measurement times at very low heating rates. Peak heat flux rates at 1 °C min^{-1} were used for the direct comparison with heterotrophic respiration based on the premise that the system at low heating rates is at thermal equilibrium (Höhne et al. 2003). To allow such direct comparison of DSC reaction rates with microbial respiration rates, energy fluxes had to be converted to CO_2 units because no microthermal methods for measuring heat fluxes of biological systems were available. To convert the DSC heat flux at peak temperature into Rh units (micrograms CO_2-C per gram OC per day), the energy content (joules per gram) of each sample was quantified as the integral over the whole thermogram. The reaction enthalpy measured by DSC was 30.8 (±1.4) kJ g^{-1} OC on average (1 SE). For calculating CO_2 fluxes from energy fluxes, the energy content of any single sample was used rather than the average number provided here. The converted heat fluxes resulted in an average flux of 1.05×10^7 ($\pm1.7\times10^6$) μg CO_2-C g^{-1} OC day^{-1} for β of 1 °C min^{-1} at the peak temperatures of the first exotherm.

Results and discussion

Temperature sensitivity of chemical oxidation

In the soils under study, mean activation energies (Ea_{DSC}) of 135.5 (SE 1.4) kJ mol^{-1} were obtained for chemically oxidized samples. Reaction rates at peak temperatures, converted to hypothetical rates at room temperature (k_{DSC25}), exhibited a significant negative correlation with Ea_{DSC} (r=−0.95; p<0.001; Fig. 1), thus obeying Arrhenius kinetics. The close relationship indicated that sample reactivity was mainly driven by the reaction temperature and that other possible factors were of minor importance. Because different soil types were measured, variability among samples may be explained by differences in OM chemistry or molecular complexity. The parameters pH, C/N ratio, and thermal stability, measured as T50, differed significantly between mineral and organic soils (P<0.05; t test), whereas ln k_{DSC25} and Ea_{DSC} did not. The latter two, however, indicated a slightly higher thermal reaction rate that was less temperature sensitive for organic compared to mineral soils that may refer to a reduction of thermal degradability due to organomineral association.

Neither ln k_{DSC25} nor Ea_{DSC} showed a statistically significant relationship with any other chemical or thermal parameter of the samples, indicating that the temperature dependency of chemical oxidation is largely independent on sample properties such as elemental contents or pH. The lack of relationship with T50 may be explained by the fact that both k_{DSC} and Ea_{DSC} were derived from the reaction rate of the first major exothermic peak, whereas the overall thermal stability relates to the degree of polymerization and is also affected by thermally more stable OM compounds (Plante et al. 2009).

Temperature sensitivity of heterotrophic respiration

On average, the catalytic effect of enzymes in living soil significantly reduced Ea from 135.5 (Ea_{DSC}) to 86.7 kJ mol^{-1} (Rh) and this effect is in agreement with our first hypothesis. However, chemical and microbial temperature sensitivities were independent of each other (r=0.18; p=0.47) (Fig. 2).

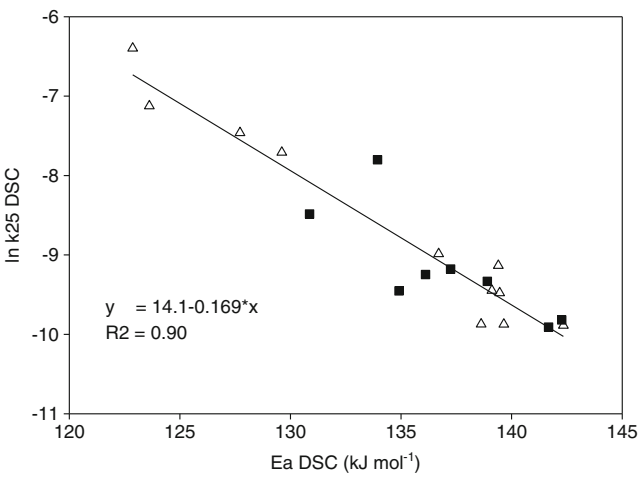

Fig. 1 Theoretical reaction rate (μg CO_2-C g^{-1} OC day^{-1}) of chemical oxidation at 25 °C as a function of the chemical activation energy Ea_{DSC}. *Solid squares* mineral soils, *open triangles* organic soils

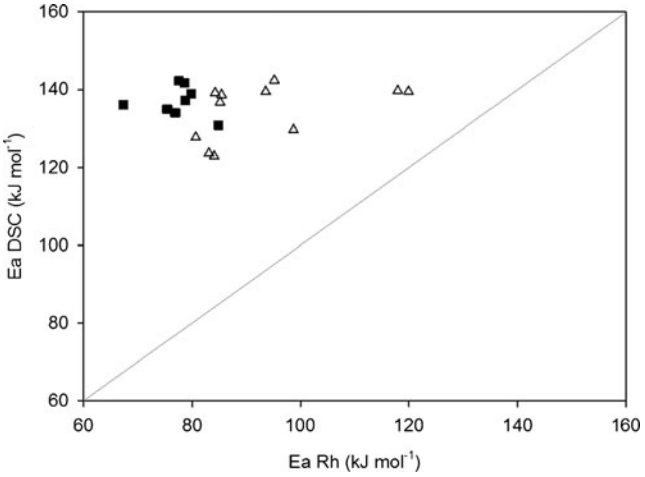

Fig. 2 Comparison of activation energies for chemical (Ea_{DSC}) and enzyme-catalyzed oxidation (Ea_{Rh}) of soil carbon. *Solid squares* mineral soils, *open triangles* organic soils

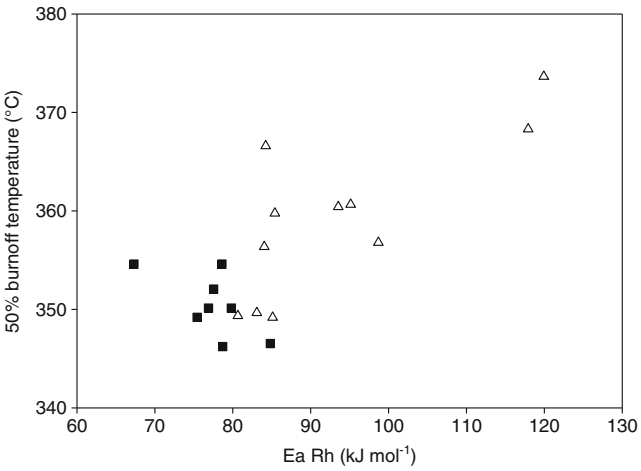

Fig. 3 Relationship between the temperature sensitivity of heterotrophic respiration rates Ea_{Rh} and the 50 % burnoff temperature, an integrated measure for thermal stability, as measured by DSC. *Solid squares* mineral soils, *open triangles* organic soils

The catalytic effect was more pronounced for mineral soils (Ea_{DSC} 137.0 ± 1.4 [1 SE], Ea_{Rh} 77.4 ± 1.7 kJ mol^{-1}) compared to organic soils (134.5 ± 2.1, 93.4 ± 4.2 kJ mol^{-1}), and thus, the hypothesized higher Ea_{Rh} in mineral soils could not be supported. The slightly smaller mean Ea found for the chemical degradation of organic soils during thermal treatment did not translate into a proportional decline in Ea for microbial decomposition. In our study, organic matter in mineral soils is probably more decomposed than that in organic, peat-forming soils because it has a high fraction of mineral-associated organic matter and a narrow C/N, indicative of a substantial fraction of microbial-derived OM (Leifeld and Fuhrer 2009). If the substrate quality is defined as being related to, i.e., negatively correlated to, molecular complexity and the number of steps needed to break down a substrate and make it available, Ea_{Rh} should increase with declining quality. Our results tentatively suggest that microbial decomposition and subsequent organomineral association need not to be associated with a decline in quality due to the much smaller Ea_{Rh} found in mineral soils.

As a consequence of the reduced activation energy, the values of k_{Rh25} were 1.5×10^7 times k_{DSC25}. In turn, temperatures of between 347 and 428 °C were required to induce chemical reaction rates of similar magnitude to those achieved by microorganisms at room temperature. Ea_{Rh} showed a highly significant and positive relationship with two measures of thermal stability, namely T50 (r=0.77; p<0.001) and the peak temperature during chemical oxidation (r=0.60, p<0.01). Figure 3 exemplifies how Ea_{Rh} increases with T50 measured by DSC. Furthermore, ln k_{Rh25} correlated significantly, but negatively, with these thermal parameters (r=−0.73; p<0.001 and r=−0.49, p<0.05 for T50 and peak temperature, respectively). These results confirm earlier findings on relationships between thermal and other chemical or microbial soil attributes (Lopez-Capel et al. 2008; Grisi et al. 1998) and imply that a large amount of thermally labile SOM compounds is favorable for microbial decay. This agrees with the argument that the first exotherm evolving from oxidation of thermally labile material is attributable to OM that is easily decomposed by microorganisms. Conversely, microbial activity seems hindered in the presence of large amounts of thermally stable material (Harvey et al. 2012).

However, the aforementioned relationship between thermal stability and decomposability by organisms does not provide robust insight into the role of activation energies of chemical oxidation for enzyme-mediated processes. This is because thermal stability parameters are not directly representing Ea_{DSC} that is measured using different heating rates. Hence, we do not regard the relationship between heterotrophic respiration and measures of thermal stability such as T50 or peak temperatures as being conclusive because we are looking for the connectivity between the temperature sensitivity of chemical and microbial oxidation. The results strongly indicate that such a causal relationship does not exist. The comparison of Ea_{Rh} and Ea_{DSC} rather suggests that they are representing different types of qualities. The inherent stability of an arrangement of molecules subject to chemical oxidation is not related to the stability experienced by microorganisms and their enzymes. Therefore, the microbial or biochemical quality of a substrate, as measured by means of respiration rates at different temperatures, must be related to additional factors other than degree of polymerization or carbon speciation as seen by the thermal method.

Furthermore, whereas the microbial oxidation rate ln k_{Rh} was not related to Ea_{DSC}, it was significantly negatively related to Ea_{Rh} (r=−0.68; p<0.01 at 25 °C, r=−0.80, p<0.001 at 15 °C). A comparable range of Ea_{Rh} values to those found in our study

and a similar negative relationship have been previously reported for a wide range of sites and soil conditions (Fierer et al. 2006; Craine et al. 2010a) and cited as evidence for recalcitrance being a major control on the temperature sensitivity of Rh. This is because a small Rh is thought to coincide with a poor substrate quality and, correspondingly, higher temperature sensitivity. The relationship between ln k_{Rh} and Ea_{Rh} (Fig. 4), however, was weaker than that between k_{DSC25} and Ea_{DSC} (Fig. 1), and some samples revealed similar k_{Rh} within an Ea range of around 70 to 100 kJ mol^{-1}, which is in contrast to the results from the chemical oxidation and the opposite of what would be expected if k_{Rh} was just a function of Ea_{Rh}. A similar respiration rate for samples with very different microbial activation energy suggests factors other than quality affect k_{Rh} and these will be elaborated in the next section. Note that k_{Rh} is normalized to soil organic carbon and, thus, to the bulk substrate concentration.

Controls on temperature dependency of heterotrophic respiration

Two chemical properties known for their important role in controlling enzyme activity and substrate decomposition by organisms in soil, pH and C/N ratio, correlated significantly with both ln k_{Rh} and Ea_{Rh} (Table 2). The enzymatic potential for oxidizing the stable fractions of SOM is strongly related to pH, whereas the enzymatic potential for hydrolyzing labile SOM components is tied to soil pH and the stoichiometry of the decomposer community (Sinsabaugh et al. 2008). The pH optima differ widely across enzymes, and pH dependency of enzyme activities can, thus, be positive or negative depending on the observed range of pH values. We found a significantly negative relationship between pH and Ea_{Rh} (Table 2) for the pH range of 3.1–5.4, whereas Craine et al. (2010b) reported converse results for mineral grassland soils in the pH range 5.4–7.6. Interestingly, merging of these data would reveal a minimum Ea_{Rh} at a pH of approximately 5.4 (Fig. 5). These combined data may indicate that different enzymes with different pH optima exert control on instantaneous rates of key metabolic processes and, therefore, different substrates contribute to the observed CO_2 flux. Recent research on pH effects on decadal to centennial SOM turnover showed a stimulating effect of declining soil acidity (pH range 3.9–5.9) on carbon turnover rates at the Alp Flix site (Leifeld et al. 2013). Hence, soil pH may control activity in the short and in the long term. In addition, soil acidity may affect not only k_{Rh} but also Ea_{Rh}, although the mechanisms behind pH effects on temperature sensitivities still need to be explored. Also, the soil C/N ratio correlated highly significantly with both k_{Rh} and Ea_{Rh} (Table 2) and with declining C/N ratios respiration rates increased while activation energies decreased. It seems reasonable to assume that particular in organic soils having a wide C/N ratio, N may be a limiting factor for heterotrophic soil respiration. However, C/N also covaried with soil pH, making it difficult to separate effects among these two.

Table 2 Correlation coefficient (Pearson) between heterotrophic respiration at 25 °C (ln k Rh), activation energy of Rh (Ea_{Rh}), C/N ratio, and pH value of soils ($p<0.001$ ***; $p<0.01$ **)

	C/N ratio	pH
ln k Rh	−0.73***	0.66**
Ea_{Rh}	0.89***	−0.75***
C/N ratio		−0.84***

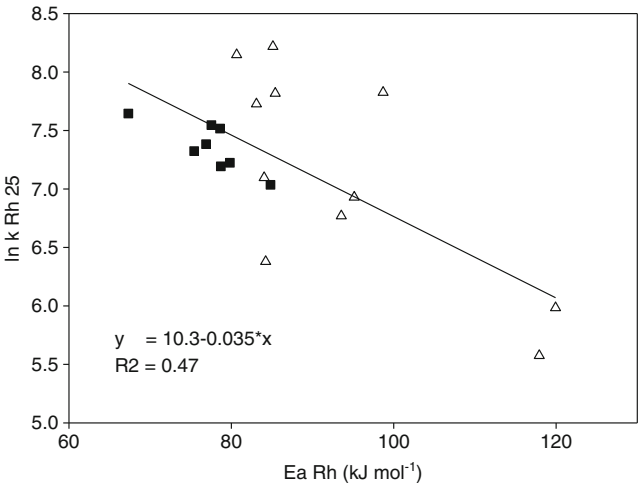

Fig. 4 Reaction rate (μg CO_2-C g^{-1} OC day^{-1}) of heterotrophic respiration (Rh) at 25 °C as a function of the microbial activation energy. *Solid squares* mineral soils, *open triangles* organic soils

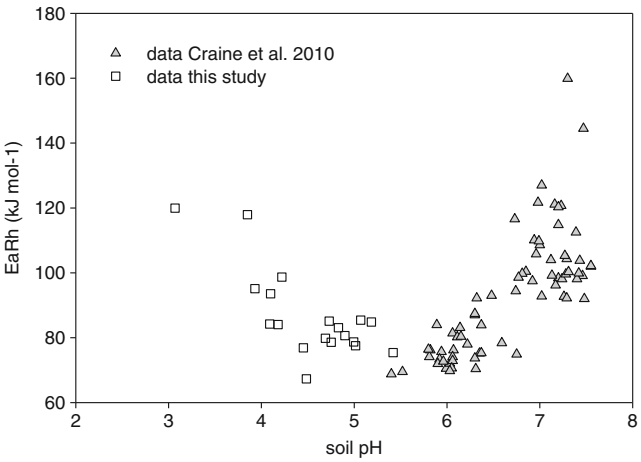

Fig. 5 Activation energy of heterotrophic respiration in relation to soil pH. Triangles represent data published by Craine et al. (2010b) for grassland sites in North America; *squares* data from this study

Conclusion

Organic matter thermal stability correlated significantly with rates and activation energies of heterotrophic respiration, confirming that SOM thermal stability can be related to biological functioning. However, the temperature sensitivity of microbial SOM decomposition is not related to the chemical activation energy of the corresponding substrate that we measured by its thermal stability against oxidation. The capacity of the decomposer community and the catalytic power of exoenzymes it releases seems to be largely independent of the substrate's inherent recalcitrance but regulated by factors such as soil pH or substrate C/N ratio, both of which are linked to the organisms' physiology and stoichiometry.

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