

Application of scanning calorimetry to estimate soil organic matter loss after fires

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Abstract The severe heating of soil during wildfires and prescribed burns may result in adverse effects on soil fertility due to organic matter loss. No rapid and reliable procedure exists to evaluate soil organic matter (SOM) losses due to heating. Enthalpy of SOM combustion correlates with organic matter content. Quartz is a ubiquitous mineral in soils and has a remarkably constant composition and reversible α – β phase transition at 575 °C. We suggest that SOM content in heated and unheated soils can be compared using the ratio of SOM combustion enthalpy on heating to the β – α quartz transition enthalpy measured on cooling of the same sample. This eliminates the need to dry and weigh the samples, making possible field applications of the proposed method. The feasibility of using the $(\Delta H_{\text{comb SOM}})/(\Delta H_{\beta-\alpha} \text{ Qz})$ ratio was established with experiments on soil samples heated in the laboratory and the method was then used for evaluation of SOM loss on two pile burn sites at UC Berkeley’s Blodgett Forest Research Station in Georgetown, California.

Keywords Soil · Fires · Organic carbon · Scanning calorimetry

Introduction

Organic matter content is a critical factor of soil quality and an important regulator of CO₂ in the atmosphere. The dry combustion method of measuring soil organic carbon

(SOC) concentration dates back to 1900 [1] and relies on quantitative analysis of CO₂ evolved on combustion of soil organic matter. Today this procedure is considered the most accurate, but the high cost of modern dry combustion instruments is a limitation to many laboratories [2]. Acid pretreatment is often required for correction for inorganic carbon from carbonate minerals present in soil samples.

A wet chemical oxidation method (sometimes referred to as “wet combustion”) was suggested in 1934 as a “procedure more rapid than others so far proposed useful for comparative purposes where no very exact determination is required” [3]. It has been used widely [4], however, it involves oxidation of soil carbon with chromic acid and is not feasible today due to the toxic wastes it generates. SOM content is often estimated as $k \cdot \text{SOC}$, where k is an empirical conversion factor which varies among soils and may reach values up to 2.0 [5]. Weight loss-on-ignition (LOI) is often used for “rapid and inexpensive” determination of SOM [6]. The recommended LOI procedure [4] includes overnight drying of the samples at 105 °C, weighing, combustion in a furnace, and final weighing. Due to chemisorbed and structural water, LOI values often exceed SOM content and soil-specific calibration is required to interpret them [2]. Concentration of soil organic matter is not uniform and depends not only on the soil type and usage but also on site-specific landscape characteristics [2].

There is an increasing need for robust and rapid quantitative measurements of fire’s effect on soils [7]. Fires can produce soil temperatures in excess of 300 °C in the case of wild forest fires and in excess of 800 °C for log pile fires [8]. Calorimetric methods have been used previously to characterize biomass [9, 10] and measure combustion enthalpies and ignition temperatures [11–14]. Here, we propose a rapid and reliable calorimetric method to estimate SOM loss from soils based on the ratio of SOM

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combustion enthalpy on heating the sample in air to the enthalpy of the β - α phase transition in quartz on cooling the same sample. Quartz (Qz, SiO₂) is the most commonly found mineral on the Earth's surface and is ubiquitously present in soils [16, 17]. On heating at ambient pressure above 575 °C, quartz reversibly transforms to a high temperature phase [18]. Decrease of this ratio ($\Delta H_{\text{comb SOM}}/(\Delta H_{\beta-\alpha} \text{Qz})$) in heated soil compared with unheated samples indicates SOM loss. The method has potential to be employed in the field since it does not require sample weighing or drying.

Materials and methods

The proposed method was developed using a soil sample (denoted as *Yolo*) in which SOM loss was induced by controlled heating in the laboratory and analyzed using thermogravimetry (TG) and differential scanning calorimetry (DSC). Based on these experiments, a thermal analysis procedure to estimate SOM loss using ($\Delta H_{\text{comb SOM}}/(\Delta H_{\beta-\alpha} \text{Qz})$) was developed and tested on samples from two pile burn sites at the UC Berkeley Blodgett Research Forest Station in Georgetown, CA.

Sample *Yolo* was collected near the University of California Davis campus. The sample core ~200 g in weight was collected from the surface to 10 cm depth. The details on characterization of this sample were reported earlier [15]. The sample was dried in a vacuum oven at 50 °C for 30 h, ground and homogenized. Portions of sample were heated in air at 300 °C for different time intervals to cause partial loss of SOM.

A Netzsch 409 thermal analyzer was used for controlled heating of *Yolo* sample and for TG and DSC measurements on all soils. The samples 10–70 mg in mass were heated to 800 °C followed by cooling to 300 °C. All experiments were performed in static air in platinum crucibles at 20 °C min⁻¹. Sensitivity calibration was performed with sapphire standard. Temperature calibration was performed by melting metal standards. Instrument software was used to determine weight loss and combustion enthalpies of soil samples.

The thermal analysis procedure developed on *Yolo* sample was tested on soil cores collected from a pile burn. A widely used fuel management technique in California, aimed at reducing the possibility of forest fires and managing biomass, is the collection of fallen or cut trees/shrubs to burn in the winter when there is little danger of starting uncontrolled fires. This fire prevention method is often referred to as pile burns. Samples were collected from pile burns conducted at UC Berkeley's Blodgett Forest Research Station, Georgetown, CA, 4 months after the burn. The location has Holland and Holland-Musick soil types. Holland samples were collected from compartment

321 and Holland-Musick samples were collected from compartment 481 [15]. Samples of Holland soil were collected from depths of 0–2.5 and 2.5–5 cm (Table 2). During collection, we did not expect the effect of the pile burns on SOM content to be so drastic and did not collect samples below 5 cm at the Holland site. However, a soil core was collected on the Holland-Musick site, which allowed analyses of samples from depths 5–7.5 and 7.5–10 cm. Samples of unburned soil were collected from 0 to 2.5 cm depth near the burn sites.

Results and discussion

SOM loss evaluation on controlled heating of *Yolo* sample

Heating of the dried sample from 200 to 800 °C in air in the TG/DSC produced weight loss ~13 wt% and a wide exothermic peak. Assigning heat effect and weight loss to SOM oxidation and removal as CO₂ and water, the SOM combustion enthalpy in the dried *Yolo* sample is calculated to be 17.1 kJ/g. In addition to the exothermic peak at 300–600 °C related to SOM combustion, all samples show an endothermic dip around 570 °C where the α - β quartz phase transition occurs. This transition is reversible and much more pronounced on cooling when all organic matter has been burned out.

Table 1 and Fig. 1 summarize the results of TG/DSC analysis on the *Yolo* sample, after drying at 50 °C for 30 h and after holding at 300 °C for 10, 30, and 60 min. During the data analysis, we assumed that all organic matter was removed from the sample after heating to 800 °C. We also neglected weight changes/heat effects due to possible oxidation/reduction of inorganic compounds including elements with variable valence state such as Fe and Mn. There were no additional DSC peaks attributed to such reactions.

The enthalpy of combustion per gram of organic matter decreased by 20% when the holding time at 300 °C was increased from 10 to 60 min. An increase in combustion onset temperature was also observed: from 301 °C in the sample annealed for 10 min to 376 °C for the sample annealed for 60 min. SOM loss in the *Yolo* sample heated at 300 °C was calculated from weight loss and combustion enthalpy per gram of sample compared to those in unburned sample (Table 1). Because of the decrease of combustion enthalpy per gram of SOM with increase of exposure time, we would expect that SOM loss from combustion enthalpy data would be overestimated. Indeed, heating of *Yolo* sample for 60 min at 300 °C results in 56 wt% SOM loss from TG data and 70 wt% loss from DSC data.

Table 1 Thermal analysis results and soil organic matter loss calculations for *Yolo* sample after drying at 50 °C and controlled heating

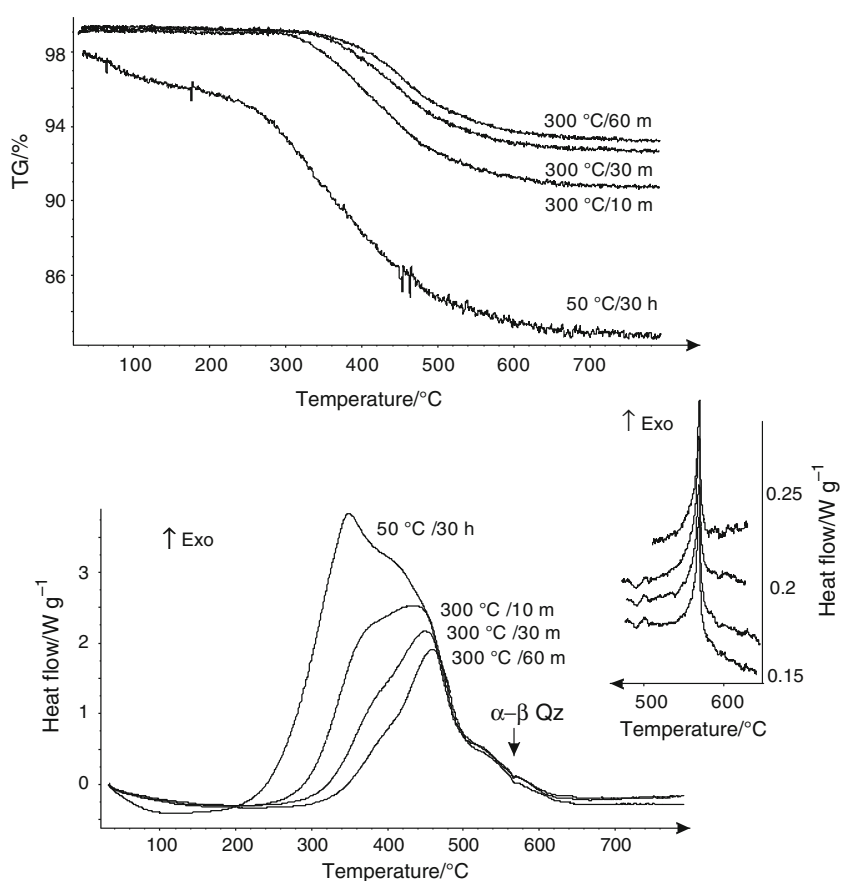
$T/^\circ\text{C}$	Time	TG/DSC analysis 25-800-25 °C ^a					$-\Delta H_c/m$ kJ/g	$-\Delta H_c/\Delta m$ kJ/g SOM	$\Delta H_c/\Delta H_{qz}$	SOM loss/wt% ^b		
		m/mg	$\Delta m/\text{wt}\%$	$-\Delta H_c/\text{J}$	$T_c/^\circ\text{C}$	$-\Delta H_{qz}/\text{J}$				TG	$-\Delta H_c/m$	$\Delta H_c/\Delta H_{qz}$
50	30 h	17.14	13.4	39.33	264	0.0423	2.3	17.1	930	0	0	0
300	10 m	25.56	8.6	31.30	301	0.0626	1.2	14.2	500	36	47	46
300	30 m	24.96	7.2	24.00	319	0.0633	1.0	13.3	379	46	58	59
300	60 m	29.12	5.8	20.20	376	0.0629	0.7	11.9	321	56	70	65

All samples were heated to 800 °C in static air at 20 °C/min

^a m is the mass of analyzed sample after drying or annealing; Δm is change in mass of sample on heating from 200 to 800 °C; ΔH_c is total enthalpy of combustion obtained by integration of exothermic peak; T_c is onset of combustion (ignition temperature) found by exothermic peak; ΔH_{qz} is enthalpy of β - α transition of quartz, measured on cooling segment

^b SOM loss calculated as $100 \times (x \text{ dried} - x \text{ heated})/(x \text{ dried})$, where $(x \text{ dried})$ and $(x \text{ heated})$ are either Δm (%) from TG, combustion enthalpy per gram of sample ($\Delta H_c \text{ m}^{-1}$), or $\Delta H_c/\Delta H_{qz}$ ratio

Fig. 1 Thermal analysis of *Yolo* sample in air at 20 °C/min. Top TG traces on heating, Bottom DSC traces on heating. Inset DSC traces showing β - α quartz phase transition on cooling. Heat treatment prior analysis is labeled next to trace



No need to weigh: $\Delta H_c/\Delta H_{qz}$ ratio

Due to the very small content of impurities in natural quartz [16], the enthalpy of the α to β transition (8.3 J/g [18]) does not vary with soil type and the observed enthalpy can be used to evaluate quartz content in any soil sample [15]. The measurement of enthalpy of transition of quartz in soils is best accomplished from the exothermic DSC peak on cooling corresponding to $\Delta H_{\beta-\alpha}$ transition,

since on heating α to β transition is masked by large exothermic peak from SOM combustion (Figs. 1, 3). No other minerals commonly found in soils exhibit reversible transitions, thus cooling traces are often not recorded on thermal analysis of soils [19].

The change in combustion enthalpy of the organic matter may be revealed using the quartz transition as an internal standard, eliminating the need to dry and weigh the samples. A decrease in the ratio of combustion enthalpy of

organic matter to enthalpy of phase transition of quartz present in the soil $(\Delta H_{\text{comb SOM}})/(\Delta H_{\alpha-\beta \text{ Qz}})$ (denoted further as $\Delta H_c/\Delta H_{\text{qz}}$) indicates organic matter loss. ΔH_c is the integrated area of the exothermic peak on heating from 200 to 600 °C and ΔH_{qz} is the integrated area of the exothermic peak on cooling due to the $\beta-\alpha$ transition in quartz. As one can see from Table 1 and Fig. 2, SOM loss calculated from $\Delta H_c/\Delta H_{\text{qz}}$ ratio is similar to that calculated from combustion enthalpy per gram of sample ($\Delta H_c \text{ m}^{-1}$),

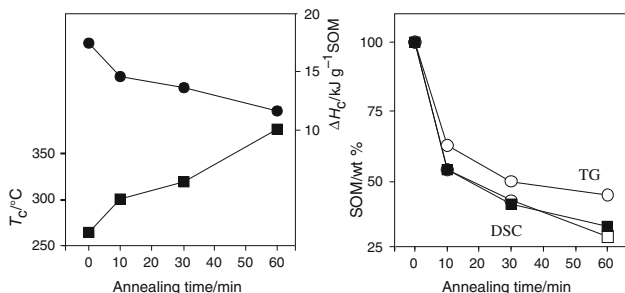
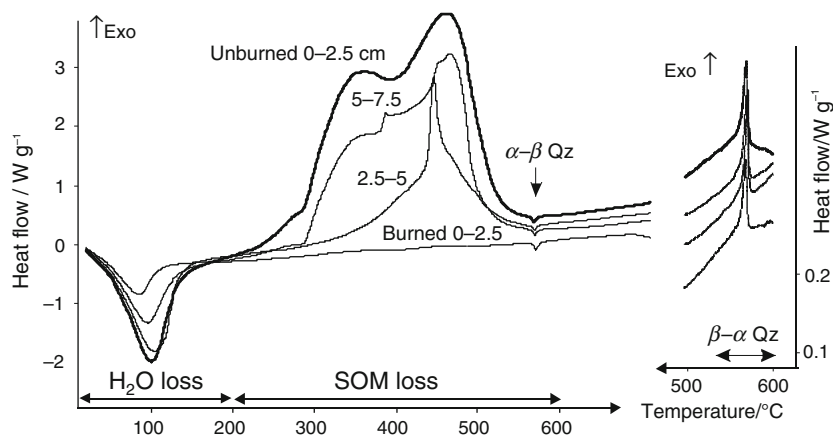


Fig. 2 Left: Change in combustion onset and enthalpy of combustion per gram of soil organic matter of Yolo sample as a function of annealing time at 300 °C. Right: Soil organic matter loss in the samples calculated from mass loss on heating (TG), from decrease in combustion enthalpy per gram of the sample (DSC open squares) and from $\Delta H_c/\Delta H_{\text{qz}}$ ratio (DSC solid squares). The values for zero annealing time correspond to unheated samples

Fig. 3 Differential scanning calorimetry traces of Holland-Musick soil type samples on heating in air at 20 °C/min. Traces for $\beta-\alpha$ quartz phase transition on cooling are shown on the inset. Control soil sample collected outside of pile burn is selected by a thicker trace



the largest difference being 7% for the sample annealed at 300 °C for 60 min.

Scanning calorimetry of soil samples from pile burn sites

A test of the application of the $\Delta H_c/\Delta H_{\text{qz}}$ ratio for estimation of SOM loss was performed on samples collected from the pile burns. No sieving or drying was performed before the analysis and soil samples were loaded field moist after removal visible leaves and roots and stones. The resulting DSC traces for Holland-Musick samples are plotted in Fig. 3 and SOM losses calculated from $\Delta H_c/\Delta H_{\text{qz}}$ ratios are presented in Table 2.

Endothermic peaks at 25–200 °C related to water loss are observed for all samples. It is not surprising since both sites were exposed to rain and then buried under snow for 4 months after burning. An unburned sample indicates higher water content than burned samples above 5 cm depth (Fig. 3). This correlates with organic matter loss in the burned samples since SOM is the most hygroscopic constituent in the soil and can hold up to 20 times its weight in water [20].

From the $\Delta H_c/\Delta H_{\text{qz}}$ ratio, more than 90 wt% of SOM was lost in the first 5 cm of soil at both sites. Substantial loss of organic matter is evident for the Holland-Musick sample at 5–7.5 cm depth. For the sample from 7.5–10 cm

Table 2 Thermal analysis of samples from two pile burns site in Blodgett Forest Research Station

Soil type	Depth/cm	$-\Delta H_c/\text{mJ}$	$T_c/^\circ\text{C}$	$-\Delta H_{\text{qz}}/\text{mJ}$	$\Delta H_c/\Delta H_{\text{qz}}$	SOM loss/wt%
Holland	Unburned 0–2.5	47094	299	128.8	366	0
	Burned 0–2.5	814	–	195.3	4.2	98.9
	2.5–5	879	–	232.5	3.8	99
Holland-Musick	Unburned 0–2.5	44900	287	74.94	599	0
	Burned 0–2.5	9.17	414	171.5	0.1	100
	2.5–5	564.1	408	85.76	6.6	98.9
	5–7.5	16822	367	79.18	212	64.6
	7.5–10	55799	289	117	477	20.4

depth, the $\Delta H_c/\Delta H_{qz}$ ratio is only 20% lower than for the unburned control sample from 0 to 2.5 cm depth. This variation may be due to decrease in SOM content with depth.

Total organic matter loss on heating is a function of heat input, exposure time, moisture content, and aeration. $\Delta H_c/\Delta H_{qz}$ can only be used as an integral indicator and cannot be distinguished among these factors. It is likely that changes in combustion onset and enthalpy per gram of organic matter can provide possibilities to reconstruct time–temperature profiles during fires, but this will require site-specific calibrations.

We want to emphasize that while knowing accurate sample mass is paramount for TG measurements and prolonged drying or measuring water content is needed for data on combustion enthalpy per gram of the sample to be meaningful, weight is not needed for calculation of the ratio $\Delta H_c/\Delta H_{qz}$. The limitation of using wt% loss from TG method or combustion enthalpy per gram of sample from DSC is that the difference in water content between burned and unburned samples will affect the results. Therefore, one would have to dry the sample first which is not practical in the field. The proposed $\Delta H_c/\Delta H_{qz}$ approach circumvents this difficulty and should be easy and fast to apply in the field if a robust portable DSC is available. Such a field application would require minimum sample preparation and portability, so one could perform the test in the field whenever a go/no-go decision needs to be made after a test burn in a prescribed burn scenario. We propose that an inexpensive field version of a scanning calorimeter operating from room temperature to 600 °C can be constructed and applied for field analysis of soil heated during wild and prescribed fires. The experiments can be conducted in static air with crucible-free loading, utilizing the ratio of peak areas related to combustion (on heating) to quartz phase transition (on cooling) to automate data collection and analysis. A Tian–Calvet [21] type calorimeter with four cells open from both ends would easily provide robustness and air circulation needed for such experiments but a conventional DSC could also be employed. In addition to proposed application for evaluation of organic matter loss after fires, DSC traces can also be used to evaluate differences in water and organic matter contents and composition between soil types and to establish site-specific sampling strategies.

Conclusions

Scanning calorimetry can be used to estimate soil organic matter loss after fires. This study indicated that the quartz present in the soils could be used as an internal standard and the $(\Delta H_{\text{comb SOM}})/(\Delta H_{\beta-\alpha} \text{ Qz})$ ratio as an indicator of

organic matter loss. This method eliminates the need for weighing and drying the sample and could be used in the field.

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