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Does Dirt Burn?
Application of Scanning Calorimetry to Estimate Soil Organic Matter Loss after Fires

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BACKGROUND

A forest fire can be thought of as a performance enhancement drug for the forest metabolism since during a fire, chemical changes that require years of microbial activity can occur within a matter of seconds. There are some side effects, however, and fire's most significant indirect effect on soil is possible decrease of the soil organic matter (SOM) content. SOM is defined as "all organic materials found in soils irrespective of origin or state of decomposition" and is a critical indicator of soil quality. SOM consists of C, H, O, N, P and S, and, since it is difficult to actually measure the SOM content, most analytical methods determine the soil organic carbon (SOC) content and estimate SOM through a conversion factor. Active SOM consists of compounds which can be consumed by microorganisms. Stabilized SOM originates from the plants that grew centuries ago, represented by humic acids, fulvic acids and humins. SOM can absorb six times its weight in water and serve as a binding agent in aggregates of soil particles.

MOTIVATION

There is a need for robust quantitative measurements of fire's effect on soils.

The goal of our present research is to evaluate the potential of differential thermal analysis and thermogravimetry techniques to characterize effects of fire-induced heating on soil. We introduce a thermal analysis method potentially applicable for field use to characterize organic matter loss after fires.

Samples Collection, Initial Treatment and Characterization

The first experiments were performed on the *Yolo* soil sample collected in Davis, Yolo County, California. The soil is a fine silty clay loam and classified (according to the USDA system) as an Aquic Paleudalf. In addition to drying and controlled annealing followed by TG/DSC analysis, mineral composition and amorphous matter content for *Yolo* sample were characterized by X-ray diffraction.

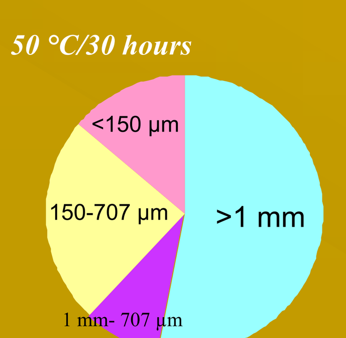
Further experiments were performed on *Holland* and *Holland-Musick* soil samples collected at an actual pile burn sites located at UC Berkeley's Blodgett Forest Research Station (compartments 321 and 481).

The piles were burned on December 17 2007. The samples of burned and unburned soil were collected on April 10, 2008. The site was covered with snow for several months before collection and some snow was still present in the forest at the time of the collection

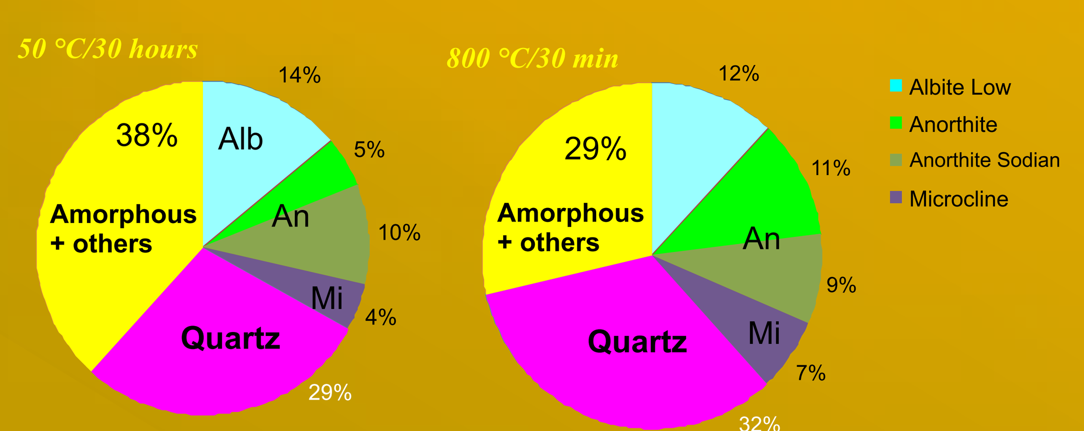
Collection of Holland sample: B - burned U-unburned control

Yolo Sample

A soil sample core ~200 grams in weight was collected from the surface to 10 cm depth. The sample was dried in a vacuum oven at 50 °C and 60 mbar and periodically weighed on a laboratory balance. The weight stabilized after 30 hours. The particle distribution was analyzed by sieving. The fraction 1 mm to 150 µm was ground and homogenized in a McCrone Spex 8000 mill using agate spheres and milling mortar. Part of the sample was heated in a furnace at 800 °C for 30 minutes, resulting in ~16% weight loss. Mineral compositions of heated and unheated samples were analyzed by whole profile refinements of powder X-ray diffraction (XRD) patterns obtained using Bruker D8 diffractometer.



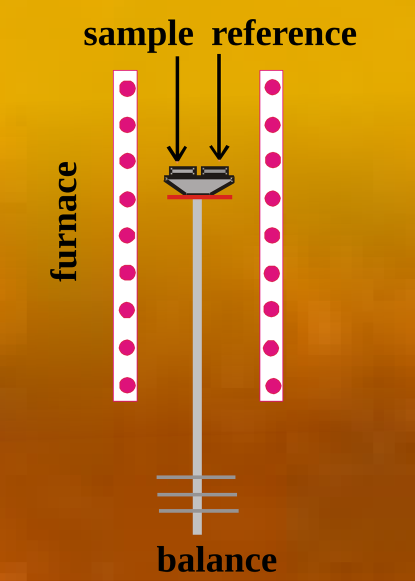
Sieving fractions



Quantitative powder XRD analysis

Observed decrease in Amorphous+others fraction by 9% after simulated burning is due to soil organic matter (SOM) loss. Despite incomplete identification of the phases which compromised the refinement slightly, this value is reasonably close to the 13% weight loss determined by thermogravimetry. However, using XRD for SOM loss characterization is not practical, due to uncertainties and constraints on sample preparation and high cost and it certainly can not be done in the field.

Thermogravimetry and Differential Scanning Calorimetry



DSC/TG trace on heating to 800 °C and cooling to room temperature were recorded on Netzsch 409 apparatus in static air at 20 °C/min. Pt crucibles with lids and samples 40-70 mg were used. Sensitivity calibration was performed from Cp of sapphire standards. Temperature calibration was performed by melting metal standards.

Yolo sample was run homogenized and ground after drying at 50 °C for 30 hours. New portions of unheated sample were further treated in the Netzsch 409 apparatus at 300 °C and 500 °C for different time intervals and then heated to 800 °C.

Holland and *Holland-Musick* samples from pile burn sites were analyzed as-collected without any heat treatment or sieving.

NO NEED TO WEIGH: ?Hcomb /?Hqz ratio

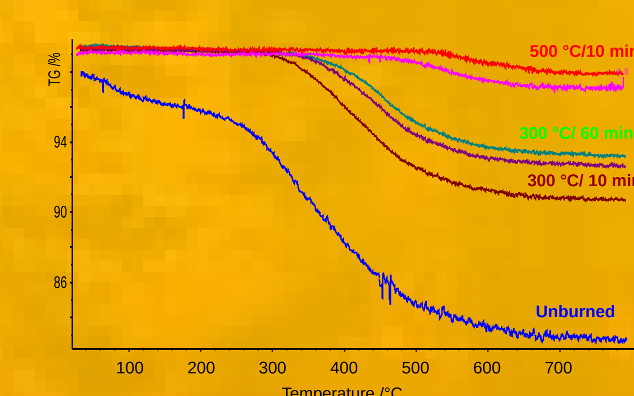
Can TG/DSC reliably test whether significant SOM loss occurred or not in a real fire situation? In order for such application to be successful, it has to require minimum sample preparation and be portable, so one could perform the test in the field whenever a go/no-go decision needs to be made after a test burn in a prescribed burning scenario.

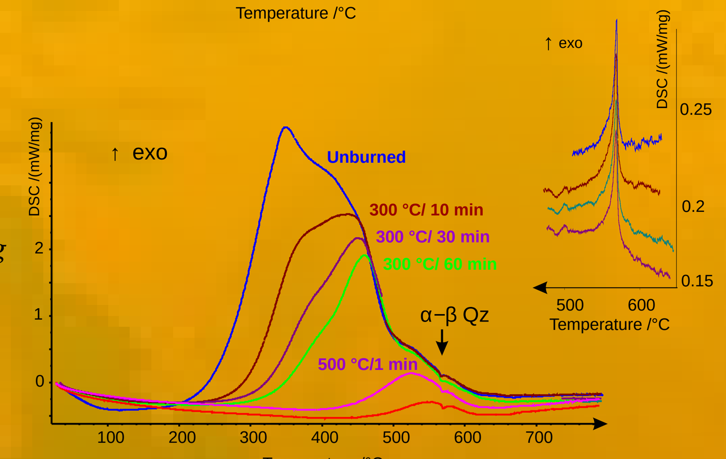
The limitation of using wt% loss from TG method or combustion enthalpy per gram of sample from DSC is that the difference in water content between burned and unburned samples will affect the results. So, one would have to dry the sample first which is not practical.

We propose to use ΔHcomb /ΔHqz ratio in the sample as the criterion for the loss of soil organic matter, where ΔHcomb is the integrated area of the exothermic peak on heating from 200 to 600 °C and ΔHqz is the integrated area of the exothermic peak on cooling due to β−α phase transition in quartz.

RESULTS *Yolo* sample

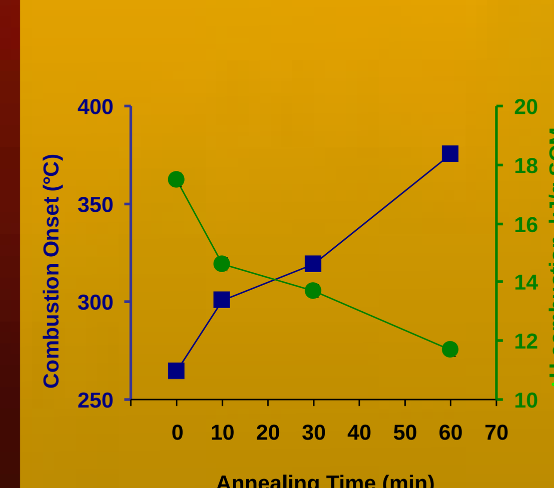
DSC show wide exothermic peaks on heating from 300 to 600 °C and a small endothermic dip around 570 °C. TG trace indicates corresponding weight loss. Since we dried Yolo sample prior to analysis, we attribute most of the weight loss and exothermic DSC peak to the combustion of organic matter. We attribute the endothermic effect at ~570 °C (on heating) and exothermic peak (on cooling) to reversible *α-β* transition of quartz present in the soil. This transition is more pronounced on cooling since on heating it is superimposed on the large exothermic effect from the combustion of organic matter.



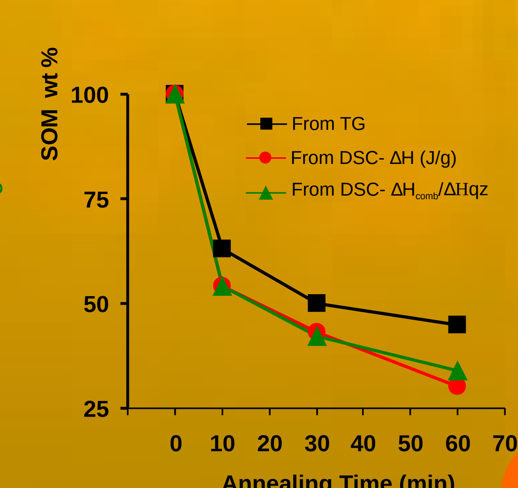


TG and DSC traces on heating of Yolo sample in air after annealing at indicated conditions..

Inset: DSC traces showing β-α quartz phase



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.



Soil organic matter loss in the samples calculated by different methods

In analyzing these results we considered that all water was removed from the sample during drying at 50 °C and all organic matter oxidized and evaporated 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.

Enthalpy of combustion per gram of organic matter can be calculated from combustion enthalpy and weight loss on heating. It decreased by 35% with increase of annealing time from zero to 60 minutes, thus we would expect that SOM loss from combustion enthalpy data would be overestimated. Indeed, heating of Yolo sample for 60 minutes at 300 °C results in 55 wt% SOM loss from TG data and 70 wt% loss from DSC data. Increase in combustion onset temperature was also observed: from 301 °C in the sample annealed for ten minutes to 376 °C for the sample annealed for 60 minutes.

TG/DSC results for *Yolo* sample heated to 800 °C after annealing at 300 °C for 10, 30 and 60 minutes.

T °C/min	TG/DSC analysis 25-800-25 °C					-ΔHc/Δm	ΔHc/ΔHqz	SOM loss (wt %)*		
	M, mg	Δm, mg (%)	-ΔHc J	Tc. on. °C	-ΔHqz β-α J	kJ/g SOM		TG	ΔHc /m	ΔHc /ΔHqz
Unburned	17.14	2.3 (13.1)	39.33	264	0.0423	17.5	**930**	0	0	0
300/10	25.56	2.2 (8.3)	31.30	301	0.0626	14.6	**504**	37	46	46
300/30	24.96	1.8 (6.5)	24.00	319	0.0633	13.7	**389**	50	57	58
300/60	29.12	1.7 (5.9)	20.20	376	0.0629	11.7	**318**	55	70	66

***calculated as 100*(Xtotal -X burned)/Xtotal** *, were Xtotal and X burned are either weight loss (TG), or combustion enthalpy per gram* $\Delta H_c/m$ *of sample, or* $\Delta H_c/\Delta Hqz$ *ratio in the samples*

m is the mass of analyzed sample after drying or annealing

Δm is change in mass of sample on heating to 800 °C

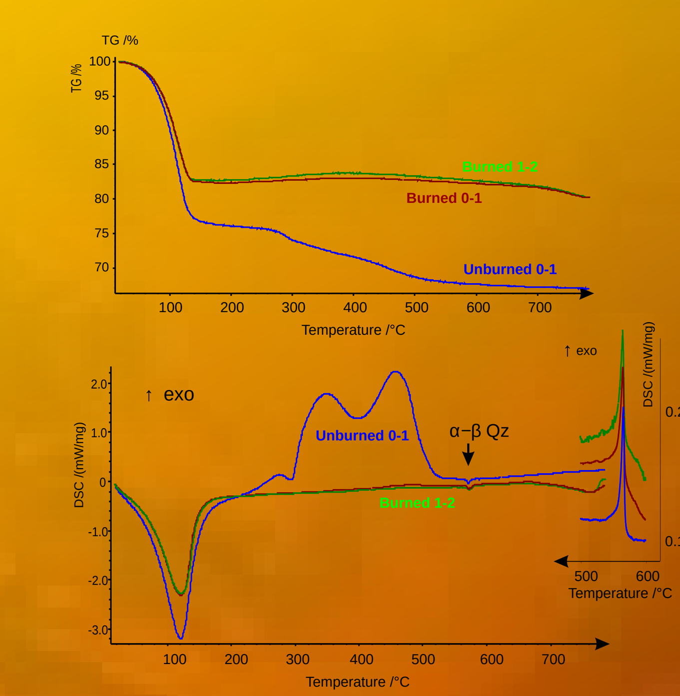
ΔHc is total enthalpy of combustion in Joules, obtained by integration of exothermic peak in 200-700 °C range

Tc. on is onset of combustion (also known as ignition temperature) from exothermic peak

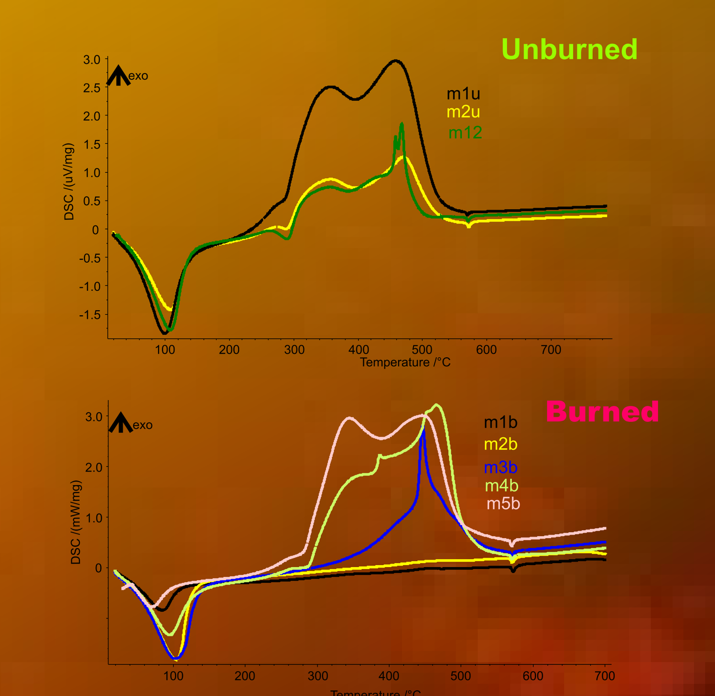
ΔHqz is enthalpy of **β-α** transition of quartz in Joules, measured on cooling segment

RESULTS

Holland pile burn site



Holland-Musick pile burn site



Holland pile burn site

Depth	?H comb mJ	-? H Quartz β−α	?Hc SOM /? Hqz
Unburned 0-1”	47 094	128.8	**366**
Burned 0-1”	814	195.3	**4.2**
Burned 1-2”	879	232.5	**3.8**
Burned 12-13”	68 870	177.4	**388**

Holland-Musick pile burn site

Depth	ΔH comb mJ	-ΔH Quartz β−α	ΔHc SOM /ΔHqz
Unburned 0-1”	44900	74.9	**599**
Unburned 1-2”	22876	79.6	**287**
Burned 0-1”	9.2	171.5	**0.1**
Burned 1-2”	564.1	85.8	**6.6**
Burned 2-3”	26911 16822 16825	152.0 79.2 76.0	**177** **212** **212**

Summary on pile burn sites samples

1. Meaningful results from ΔHcomb /ΔHqz ratio from limited number of experiments on 40-70 mg samples without any prior treatment !
2. More then 80 % of soil organic matter lost for first two inches depth on pile burn sites studied.
3. Decrease in SOM content in unburned soil with depth and topographic features should be taken into account when interpreting data on SOM loss.

CONCLUSIONS AND FUTURE WORK

Scanning calorimetry can be used to estimate soil organic matter loss after fires. We propose using quartz present in the soils as internal standard and ΔHcomb /ΔHqz ratio as organic matter loss indicator. This method eliminates the need of weighing and drying the sample.

It is proposed that a portable field version of a scanning calorimeter operating from room temperature to 700-800 °C can be constructed and applied for field analysis of soil heated as result of wild and prescribed fires. The experiments can be conducted in static air with crucible-free loading utilizing the ratio of peaks related to change in combustion (on heating) to quartz phase transition (on cooling) to automate data collection and analysis. A Tian-Calvet type calorimeter with two or four cells open from both ends would easily provide reproducible sample size and air circulation needed for such experiments but a conventional DSC could also be developed.

ACKNOWLEDGEMENTS

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