Short Communication

THERMAL ANALYSIS OF MINERAL SOILS BEFORE AND AFTER OXIDATION WITH SODIUM HYPOCHLORITE

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The nature of recalcitrant organic carbon (OC) in soil is a matter of great debate and various chemical treatments exist for its isolation. We compared calorimetric properties from silt+clay fractions of eight mineral soils by means of DSC before and after chemical oxidation with sodium hypochlorite (NaOCl) to find out, whether recalcitrance of soil organic matter against chemical oxidation coincides with its thermal stability. NaOCl oxidized around 75% of the OC, which corresponded well to a mean loss in heat of reaction of 80%. Peak temperatures and 50% burnoff temperatures did not change systematically after oxidation showing that the thermal stability of NaOCl residues was similar to that of untreated samples. Three samples revealed peaks at >520°C after oxidation indicative for the presence of pyrogenic carbon.

Keywords: DSC, mineral soil, NaOCl, stable organic matter

Introduction

The nature and stabilisation mechanisms of recalcitrant organic carbon (OC) in soil are a matter of great debate because soils contain about twice the carbon present in the atmosphere and are considered important terrestrial carbon sinks [1]. Various chemical protocols exist to isolate stable OC out of the bulk soil. Sodium hypochlorite (NaOCl) has been used to isolate a chemical resistant OC fraction that is bond to mineral surfaces [2]. The treatment is presumed to cleave all methane, methylene, and methyl groups [3]. Radiocarbon dating of the material remaining after NaOCl oxidation showed that it is not only chemically resistant, but has also long residence time in soil [4]. Oxidation with NaOCl is considered to remove lignin from environmental samples preferentially, thus allowing for the quantification of condensed aromatic structures such as black carbon in soil by eliminating overlapping signals from phenols in NMR spectra [5].

The thermal stability of soil organic matter (SOM) depends on land-use and management [6]. For sites under contrasting agricultural land-use, Lopez-Capel *et al*. [7] showed that free and intra-aggregate light fractions of SOM were characterized by typical thermal responses and that thermal and chemi-cal attributes of the organic matter were correlated. Clay fractions in chronosequences from native forest to long-term bare fallow differed in their thermal stability and the bare fallow was relatively enriched in stable organic matter [8]. Also long-term depletion of labile OC in fertilisation experiments increased the thermal stability of the remaining SOM significantly [9]. Based on these findings we hypothesise that the thermal stability of NaOCl-residues is different to that of the untreated soil.

Experimental

We took eight mineral soil samples from the Swiss National Soil Survey Programme. Each sample is composed of 50 cores taken from all sites within a plot of $10 \cdot 10$ m between 1985 and 1991. A detailed description of the sampling technique together with individual site characteristics such as climate, geology and land-use can be found in Vogel *et al*. [10]. Silt+clay fractions were isolated by physical fractionation after ultrasonication with 22 J mL^{-1} soil suspension, and fractions <63 μm were treated with NaOCl according to Kaiser and Guggenberger [2]. Table 1 shows basic site and sample properties.

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Table 1 Basic characteristics of soil samples in the study. Values refer to the fraction <63 μm (i.e. silt plus clay fraction). MAT (mean annual temperature)

	Land-use	Geology	MAT/°C	Depth/cm	Clay/%	OC/%
26AV	arable	moraine	+9.2	0–20	42	2.14
29EBO	meadow	moraine	+8.3	0–20	49	2.84
30EK	meadow	sandstone	+8.3	10–20	38	2.66
37EP	meadow	moraine	+7.7	10–20	34	2.55
49US	meadow	flysch	+5.4	0–5	54	7.32
50RA	pasture	gneiss	–0.2	10–20	10	3.17
96GUD	vineyard	granite	+10.6	0–20	33	10.64
100MR	meadow	mica schist	–1.6	7–18	30	3.85

Curves were scanned with a differential scanning calorimeter DSC100 (TA Instruments) after heat flow calibration with sapphire and temperature and heat calibration with the melting of indium [11]. In a range of previous experiments, we tested the dependence of the DSC parameters (heat flow, onset- and peak temperatures, and heat of reaction) on different sample C concentrations and derived an optimum sample mass of 0.2 to 0.5 mg C. The finely ground and dry material was weighted into an open aluminium pan. An empty Al-pan served as the reference. Samples were heated under a flow of synthetic air of 50 mL min^{-1} from room temperature to 600°C at a heating rate of 20°C min^{-1}. DSC parameters used to characterize the stability of the materials were peak temperatures (°C), peak heights (W g^{-1} soil), total heat evolved (ΔH, J g^{-1}), and 50% burnoff temperatures (°C). Peak heights were measured as the maximum deviation from a linear baseline drawn between 150 and 568°C.

Differences between untreated and oxidized samples were analysed by a paired t-test and correlation was calculated with the Pearson's correlation coefficient.

Results and discussion

Results of the DSC runs before and after oxidation are summarised in Table 2. Mean peak temperatures were 329 and 316°C for the first, and 420 and 408°C for the second exotherm before and after oxidation, respectively. Chemical oxidation affected neither peak temperatures nor 50% burnoff temperatures significantly (paired t-test), though single peaks differed by up to 60°C. Heat of reaction for both untreated and chemically oxidised samples correlated highly significantly with the amount of OC in the sample (r=0.99, P<0.0001) in accordance with previous findings [9]. Consequently, also the percentage of OC oxidized correlated highly significantly with the reduction in ΔH due to chemical oxidation (Fig. 1). For most of the samples chemical oxidation reduced the OC content approximately six percent more than the heat of reac-

tion as can be seen by the deviation from the 1:1 line. The amount of organic matter oxidized was not related to peak temperatures or 50% burnoff values. However, the thermally and chemically most stable sample (96GUD, Fig. 1) was the one with the highest peak and 50% burnoff temperature. Peak heights of the first and second exotherm decreased on average by 82 and 78%, respectively, with no significant difference between them.

For three out of eight samples (26AV, 29EBO, 30EK), NaOCl oxidation uncovered a new exotherm at temperatures between 524 and 538°C. Figures 2 and 3 compare a sample without and with the occurrence of the new exotherm. Evaluation of the signal intensities of the new exotherm and of the non-oxidized sample at the temperature of the new exotherm revealed that the signal intensity of the untreated sample was between seven and eleven-fold higher than that of the NaOCl residue.

We hypothesised, that the thermal stability of NaOCl-residues, as measured by peak temperatures and 50% burnoff values is different to that of chemially untreated mineral soils. Our findings, however, show that there is no systematic shift in the thermal stability after oxidation, though between 60 and 95% of the OC was removed. Based on literature find-
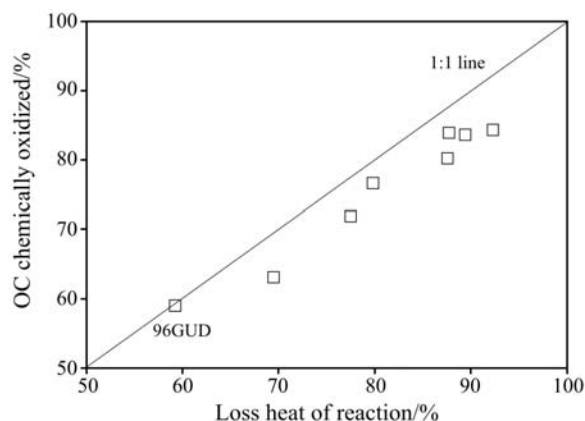
Fig. 1 Loss of OC *vs*. loss of ΔH after chemical oxidation (%)
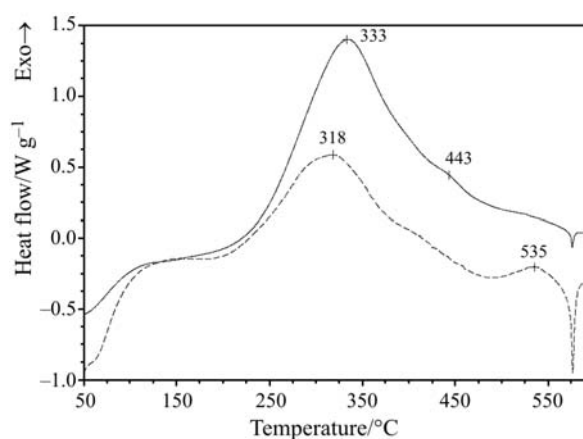
Table 2 Thermal parameters of samples before (B) and after (A) oxidation with NaOCl. Peak 1 peak temperature first exotherm (°C), peak 2 peak temperature second exotherm (°C), 50% burnoff temperature (°C), ΔH heat of reaction (J g^{-1}). Sample 26AV had no detectable second exotherm after chemical oxidation

	Peak 1		Peak 2		50% burnoff		ΔH	
	B	A	B	A	B	A	B	A
26AV	338	320	439	n. d.	346	331	510	39
29EBO	333	318	443	412	347	320	643	80
30EK	329	318	446	458	346	333	604	64
37EP	330	322	444	458	340	338	567	70
49US	329	299	397	382	345	329	1794	363
50RA	303	303	365	366	324	332	924	282
96GUD	351	312	456	396	383	345	2454	1000
100MR	315	334	374	387	332	349	1009	227
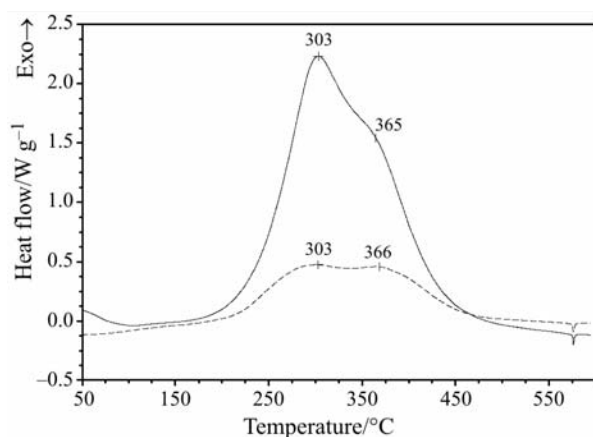
Fig. 2 Heat flow of untreated (solid) and NaOCl-treated (dashed) soil fraction <63 μm, sample 50RA

Fig. 3 Heat flow of untreated (solid) and NaOCl-treated (dashed) soil fraction <63 μm, sample 29 EBO. Heat flux of the oxidized sample is magnified 5-fold

ings that chemical oxidation residues are much older and thus more stable in soil [4], the results indicate that thermal oxidative stability of SOM does not coincide with chemical oxidative stability. Resistance of organic matter *vs*. chemical oxidation was explained by the protective capacity of poorly crystalline Fe and Al-oxides in soil [2]. This sorptive protection is also regarded an important stabilisation mechanism against biochemical degradation of organic matter in mineral soils [12], but seems to play no major role for the thermal stability of organic matter.

Treatment with NaOCl has been recommended to remove lignin from soil that otherwise would hinder NMR-based quantification of condensed aromatic compounds in environmental samples. In their study, Simpson and Hatcher [5] also showed that the oxidative agent does not preferentially attack quantitative important moieties such as alkyl C or O-alkyl C. Their finding is in line with the relatively unchanged position of peaks after NaOCl treatment in our experiment. Thermal stabilities of ordered aromatic molecules on the other hand, as occurring in coal char, soot, or some

coals are typically higher [13–15] than that of organic matter without pyrogenic or coalification history [8, 9]. Three of our samples revealed a small peak at temperatures distinctly above 500°C after NaOCl treatment. We suggest that the chemical oxidation successfully removed other organic matter, thereby uncovering that peak that is likely to derive from black carbon or other condensed aromatic structures.

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