Characterisation of Terra Preta soils and chars by thermal analysis-quadrupole mass spectrometry

E Lopez-Capel & D.A.C. Manning.
School of Civil Engineering and Geosciences, University of Newcastle, Newcastle uponTyne, NE1 7RU, UK
elisa.lopez-capel@ncl.ac.uk,

Introduction

The artificial addition of black carbon derived from combustion of plant material from pyrolysis and biofuel materials from other sources beneficially modifies the properties of soils, improving soil fertility, stabilisation and productivity and storing carbon in the soil as means of mitigating global warming (Lehmann et al, 2006). Understanding the processes and functions which black carbon influences within a soil requires many different investigative techniques. In this paper we report the use of thermal analysis-differential scanning calorimetry (TG-DSC) coupled to on-line evolved gas analysis (a) to quantify proportions of different organic matter components and (b) to describe the chemical environment of carbon, nitrogen and water within treated and untreated soils..

Thermal analysis gives a direct measurement by weight of components of soil that decompose at different stages in a heating cycle. For soil organic matter, weight losses between 250-350°C correspond to labile material, 350-500°C to recalcitrant and 500-650°C to refractory OM BC-like materials (Lopez Capel et al, 2005a, 2006). Using this approach, Terra Preta soils can clearly be distinguished without substantial sample preparation, and are enriched in recalcitrant organic matter, as would be expected.

The general aim of this work is the characterisation of soil organic matter and chars, and the description of the main transformations exerted by soil amendments (such as the incorporation of charcoal and other materials to Terra Preta soils). The formation of new forms of C highly resistant to oxidation has environmental implications in the stabilisation of C in soil, C incorporation, and for global C and N cycles.

Soils affected by forest fire in Aznalcollar, B3 site in 2004 (after a fire) and 2006

Soil, the Bane of Modern Amazonia http://www.anthonares.net///tropical_soil.jpg

Thermal analysis laboratory at Newcastle UniV.

Materials and Methods

The samples described in this paper are: Terra Preta (tp) soils and adjacent Oxisols (ox) supplied by Johannes Lehmann and coworkers; and fire affected soils collected from southern Spain supplied by Francisco J Gonzalez-Vila and co-workers

Black C-rich Anthrosols or Terra Preta soils (tp) and adjacent Oxisols (ox) soils were sampled from four archaeological sites, Hatahara (HAT), Lago Grande (LG), Acutuba (ACU), and Dona Stella (DN), near Manaus, Brazil (3°8'S, 59°52'W, 40-50 m above sea level), which have been dated to span from about 600 to 8700 yr (Table 1; modified from Neves et al , 2003, and Liang et al, 2006).

Soils from an area frequently affected by fires in the Sierra de Aznalcollar, within Seville's Sierra Norte (Southern Spain), were collected in 2006. Aznalcollar samples were as follow: Control-212, B1-214 (burn 1997 & 2004), B2-215 (burn 1997 & 2004), and B3-216 (burn 1984 and 2004)

Analysis of whole soil samples is presented here. Physical and chemical properties of the Terra Preta soils is shown in table 1.

TG-DSC-QMS evolved gas analysis was carried out by simultaneously coupling the TG-DSC system through an adapter head in the STA 449C Jupiter gas outlet via a 200°C heated capilliary to a Netzsch Aeolos QMS 403C quadrupole mass spectrometry system (*m/z* range 10 – 300). Approximately 60 mg of soil were placed in an Al_2O_3 crucible. Samples were heated at a heating rate of 20 °C min^{-1}, from ambient temperature to 1000 °C under flowing 20% oxygen in helium (50 cm^3 min^{-1}).

For QMS analysis, mass/charge (*m/z*) values from 10 to 300 were collected and *m/z* intensities of interest (12 (C), 18 (H_2O), 26 (CN), 27 (HCN), 30 (NO), 44 (CO_2 & N_2O), 45 ($^{13}C^{16}O_2$) and 46 (NO_2)), were reported.

Results

Relative proportions of labile (Exo1), recalcitrant (Exo2) and refractory or BC-like materials (Exo3) soil organic matter in Anthrosols and adjecent soils are given in Table 1.

Table 1. Physico-chemical properties, Thermogravimetry (Exo), Differential scanning calorimetry (DSC), and gas analysis (m/z) of Anthrosol and adjacent soils.

Site	Soil Type	Depth (cm)	Age (yr)	Clay%	pH (1:2:5 H_2O)	Org. C (mg g^{-1})	Total N (mg g^{-1})	C/N	Exo 1 (%)	Exo 2 (%)	Exo 3 (%)	Max T° (DCS)	Max T° (mz/44)
Hatahara (HAT)	Anthrosol (tp)	43-69	600-1000	27.0	6.4	22	1	23	18.80	54.18	27.02	451	463
Hatahara (HAT)	Adjacent soil (ox)	0-10	600-1000	35.9	4.6	21.8	1.6	14	24.97	47.99	27.04	346	403
Lago Grande (LG)	Anthrosol (tp)	0-16	900-1100	22.6	5.9	31.5	1.8	18	24.26	56.04	19.70	462	483
Lago Grande (LG)	Adjacent soil (ox)	0-8	900-1100	26.7	4.2	17.5	1.3	14	40.33	43.84	15.83	374	373
Acutuba (ACU)	Anthrosol (tp)	48-83	2000-3000	10.4	5.6	15.7	1	16	26.49	54.64	18.87	483	513
Acutuba (ACU)	Adjacent soil (ox)	0-30	2000-3000	8.5	4.7	15.4	0.8	20	35.31	51.41	13.28	351	373
Dona Stella (DN)	Anthrosol (tp)	190-210	6700-8700	0.3	5	16.5	1.1	15	23.78	51.05	25.17	496	538
Dona Stella (DN)	Adjacent soil (ox)	0-12	6700-8701	0.3	3.9	10.2	0.4	27	26.73	48.32	24.96	392	508

Results and discussion

Thermogravimetric parameters determined a higher proportion of recalcitrant and refractory SOM in Anthrosol soils than in adjacent soils (See Table 1 and Figure 1).

The DSC traces for the Terra Pretta samples (tp) very clearly show the addition of black carbon as a sharp peak corresponding to the exothermic decomposition of recalcitrant organic matter. Corresponding adjacent oxisols (ox) have a much broader peak, at lower temperatures, reflecting the decarboxylation of dominant labile materials (Figure 2). Maximum peak temperatures of Terra Pretta soils (associated with recalcitrant carbon) increase with sample age, reflecting carbon stabilisation (from 450 to 496°C). The DSC traces are mirrored by the evolution of CO_2 (Figure 3), which clearly demonstrates the presence of recalcitrant OM (max. Temp 463-535 °C). Evolved gas analysis of H_2O shows loss of moisture (100 °C), decarboxylation (350 °C), and decomposition of oxy-hydroxide clay minerals (500 ° C) (Figure 4). Evolved gas analysis of nitrogen species was limited and is not shown here.

The implication for Terra Preta soils is that the addition of charcoal to soils adds nitrogen in a slow turnover reservoir. For a better understanding of nitrogen redistribution in samples containing high percentages of recalcitrant SOM forms, we include in this study examples from chars from Southern Spain (Figure 5). Forest fires produce significant changes in soil organic matter composition, including an increase in long-lived black carbon. Evolved gas analysis of nitrogen species shows a redistribution of nitrogen species towards more recalcitrant SOM forms (Figure 6), restricting N to recalcitrant SOM fractions NO, with (mz 30)(reflecting pyrrolic or pyridinic N) at higher temperatures than for unburnt soil. Similarly, evolution of CN (mz 26) from labile SOM (amine N) is reduced by burning.

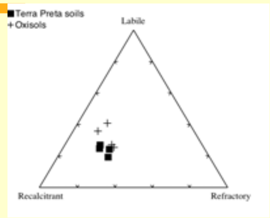

Figure 1. Thermogravimetric (TG) parameters determining proportions of labile, recalcitrant and refractory SOM in Anthrosol soils than in adjacent soils

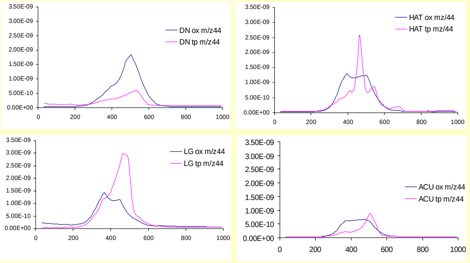

Figure 3. Thermograms of ion current *m/z* 44 (CO_2) for Anthrosols and adjacent soils

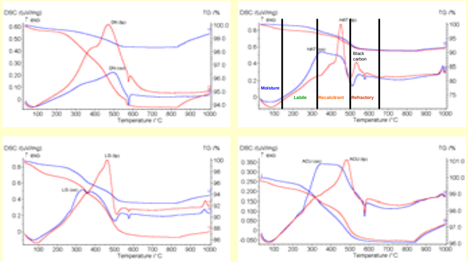

Figure 2. Thermogravimetric (TG) and differential scanning calorimetric (DSC) traces of Terra Preta and adjacent soils

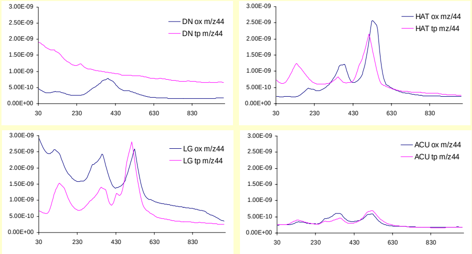

Figure 4. Thermograms of ion current *m/z* 18 (H_2O) for Anthrosols and adjacent soils

Conclusions

Thermal analysis results indicates changes in the composition of SOM in Terra Preta soils and in soils affected by forest fire as compared to adjacent and un-burn soils, respectively.

Thermal analysis allows the proportions of SOM pools to be quantified, and demonstrates the potential value of the coupled TG-DSC-QMS system for determining C and N changes in soils.

Further analysis by TG-DSC-IRMS would help identify the source of recalcitrant and refractory SOM, whether is of intrinsic or anthropogenic origin.

Information obtained from this study could be applied to studies in carbon incorporation and the use of soils as C sinks.

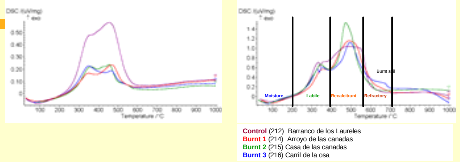

Figure 5. Thermogravimetric and differential scanning calorimetric profiles of a control and a burned soil from Aznalcollar (Spain)

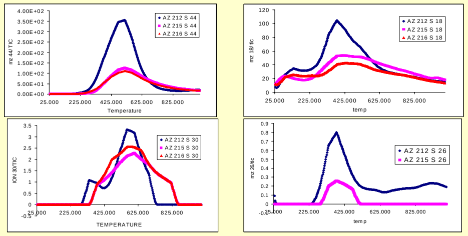

Figure 6. Thermograms of ion current *m/z* 44, *m/z* 18, *m/z* 30 and *m/z* 26 for Anthrosols and adjacent soils

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