

Novel use of thermal analyses to meet soil C monitoring in agriculture

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Abstract

Concerns exist about the application of the current methods where total organic carbon (TOC) analytical data is extrapolated from very small sample aliquots to quantify significant land areas. Extending the limits that allow larger amounts of soil to be determined for TOC assists in smoothing natural variability as well as reducing costs. Furthermore, soil carbon (C) comprises a range of organic matter (OM) with varying residence times. The main types can be characterised by different ignition temperatures allowing carbon pools to be distinguished for varying soils using thermal techniques. The added reliability and information rendered can support infrared measurements which can also be used to differentiate carbon.

Key Words

Soil carbon monitoring, dry combustion, soil carbon characterisation, thermogravimetric analysis

Introduction

A major obstacle to realising broad scale soil C monitoring is the uncertainty of how representative soil C analyses are of a larger area or indeed the near neighbourhood (Goidts *et al.* 2009). Contributing to this has been the need for sample processing (drying, grinding, sieving, splitting etc.) to isolate the fine C rich fractions. For these reasons, huge emphasis has been directed towards the most reliable and cost effective analytical methods to quantify soil carbon. This aspect can be much improved by scaling up the amount of soil material processed for each C determination. Even then, spatial statistical analysis methods are a vital component and should additionally assist in managing costs. An important goal is the capacity to estimate with confidence, from a fixed set of data, the C contribution from an entire parcel of agricultural land. Different farming practices can then be assessed in terms of their effectiveness on long term soil carbon management.

Thermogravimetric analysis (TGA) has traditionally been used to characterise chemical decomposition of materials and can be done in oxidative and inert atmospheres. In soil science, it has been widely used for the mineral fraction but for soil C applications it offers inadequately tested potential where dehydration, denaturing or oxidation report as separate events. For this type of application, qualitative analyses are the obvious outcome but quantification of organic matter is an achievable aim also. It appears that dehydration and carbonate decomposition are energy rather than time dependent (Kasozi *et al.* 2009), lending the technique to resolution of these constituents as well as organic matter, on the basis of temperature.

Methods

Sampling was done with a 3.78mm (i.d.) push/vibra corer. Soils were extruded and placed in PVC split-tubing for air drying before sectioning into horizons (0-10 cm 11-20 cm etc.) and processing in the generally accepted ways (McKenzie *et al.* 2000). The cross-sectional areas of the aliquots removed with the probe could then be used as a pro rata to determine C values for the larger stratum. To maintain comparability in the 3rd dimension, equal weights were collected and then submitted for TOC and TGA analysis.

Total organic carbon determinations were initially carried out with a vario Max CN (Hanau, Germany) elemental analyser (EA) on samples in the range 0.5 to 0.75g range. As EA is an accepted standard for % C determination, it formed a basis for comparisons. Experimentation was carried out on as large amounts of soil as feasible using a post-combustion gas analysis technique.

TGA analyses were conducted on a TA Instruments 2950 supplied with either a N₂ or O₂ atmosphere. The temperature program involved ramping to 200°C over 10 min. followed by a further ramp to 700°C over 50+ min.

Results

Comparisons were made between combustion methods applied to identical soils (homogeneity and treatment). EA and TGA were correlated and indicated the need for refinements to the C to OM conversion factor (exceeded 1.8) which in much of the loss on ignition (LOI) work has also been regarded as too low (Sutherland 1998). However TGA can be considered a quasi LOI that provides a wealth of additional information. Occurrence of mass-loss events within the organic groups could be manipulated by varying the temperature ramps and atmospheric composition. These preliminary TGA results indicated that a combination of analyses using oxidising and non-oxidising atmospheres reveals interesting differences in the spectrum of carbonaceous soil constituents. An example of a soil with 2% organic C is shown on Figure 1. The falling curve plots the absolute mass loss while the peak trace results from the differential mass change and this is sensitive to heterogeneity in the organic composition. The thermal pattern is similar to that derived by Laird *et al.* 2008. Similar to EA, the TGA microbalance and system as a whole is limited to very small amounts of material, usually in the range of 100 mg. Such small sample sizes may be disadvantageous for quantification in soils but is compensated with mass spectral data on carbon species.

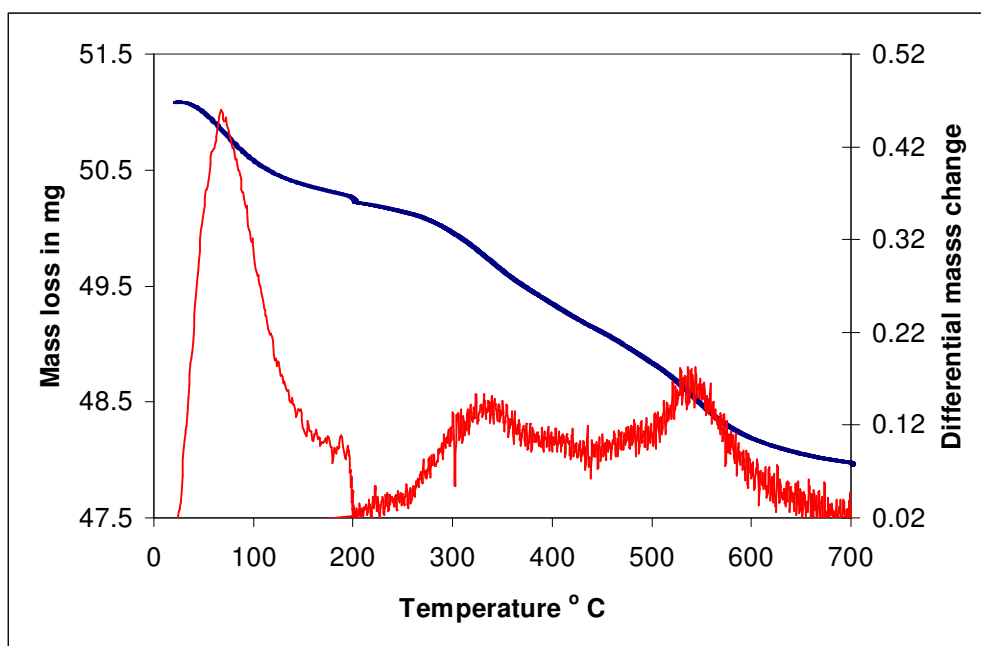


Figure 1. Loss of H₂O indicated between ambient and 200°C followed by two pulses of OM loss over 250 to 650°C.

Conclusions

Thermal methods still serve as among the most reliable carbon analysis methodologies although, indirect determinations provide speed and cost benefits. Scaling up the amount of soil carbon that can be oxidised will be an important factor in the smoothing of the inherent variability found in most soils and should assist in cost reductions. TGA has played an integral part in developing an improved set of analytical tools and provided further insights into soil C.

While carbonates commonly form part of soil C, these early experiments have focused on carbonate free soils to limit the number of variables to organic C types. Continuation of this work with a wider analytical scope will include inorganic C as it is legitimate to include this component when monitoring soil C on farms.

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