ORIGINAL ARTICLE

Soil carbon determination for long-term monitoring revisited using thermo-gravimetric analysis

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Abstract

Soils and the vadose zone are the major terrestrial repository of carbon (C) in the form of soil organic matter (SOM), more resistant black carbon (BC), and inorganic carbonate. Differentiating between these pools is important for assessing vulnerability to degradation and changes in the C cycle affecting soil health and climate regulation. Major monitoring programs from field to continent are now being undertaken to track changes in soil carbon (SC). Inexpensive, robust measures that can differentiate small changes in the C pools in a single measurement are highly desirable for long-term monitoring. In this study, we assess the accuracy and precision of thermo-gravimetric analysis (TGA) using organic matter standards, clay minerals, and soils from a national data set. We investigate the use of TGA to routinely differentiate between C pools, something no single measurement has yet achieved. Based on the kinetic nature of thermal oxidation of SC combined with the different thermodynamic stabilities of the molecules, we designed a new method to quantify the inorganic and organic SC and further separate the organic biogeochemically active SOM (as loss on ignition, LOI) from the resistant BC in soils. We analyze the TGA spectrums of a national soil monitoring data set ($n = 456$) and measure total carbon (TC) using thermal oxidation and also demonstrate a TC/LOI relationship of 0.55 for soils ranging from mineral soils to peat for the United Kingdom consistent with previous monitoring campaigns.

Abbreviations: BC, black carbon; BS, Bangor standard; FTIR, Fourier transform infrared; IC, inorganic carbon; LOI, loss on ignition; OM, organic matter; SC, soil carbon; SOM, soil organic matter; TC, total carbon; TGA, thermo-gravimetric analysis; TML, thermal mass loss.

1 | INTRODUCTION

Soil contains the largest terrestrial carbon (C) pool. Its C content plays an important role in soil health, the global C

cycle, and climate change (Amundson, 2001; Lal et al., 1998). Relatively small changes in soil carbon (SC) stocks represent important changes for the mitigation or exacerbation of climate change. However, SC is not a single homogeneous material, it is composed of organic and inorganic carbon (IC), and the organic C is distributed in pools that range in their resistance to breakdown and turnover. As a result, C pools play different roles over different timescales that impact soil health and climate regulation. No single measurement method routinely provides an assessment of these different pools. Three approaches are usually used in monitoring to assess SC, chemical oxidation such as Walkely–Black (Walkley & Black, 1934), total carbon (TC) using thermal oxidation (Allison, 1965), and soil organic matter (SOM) using loss on ignition (LOI; Nelson & Sommers, 1996).

Differentiating SC into different pools becomes increasingly challenging as illustrated in Figure 1. (1) Chemical oxidation is used to determine organic C but measures some combination of SOM + black carbon (BC) and (2) thermal oxidation measures SOM + BC + IC, while (3) acid pretreatment measures SOM + BC and (4) conventional thermo-gravimetric analysis (TGA) is often performed at $550°C$ (LOI_{550}) for 3–6 h, it has the advantage that it is fast and consequently has a very throughput; however, LOI_{550} gives consistently higher values than LOI measured at lower temperatures (Ball, 1964), This is because LOI_{550}, like chemical oxidation, measures some combination of SOM + BC. (5) The new TGA protocol separates out the SOM, BC, and $CaCO_3$ pools in a single measurement.

Why is it important to differentiate between C pools? Because different C pools have different earth system functions and turnover times. Managing soils for climate regulation requires effort to prevent C loss and build organic or inorganic stocks. Although management for soil health is focused on building SOM, the resistance of the C to degradation is critical as it influences soil aggregation (Nelson & Sommers, 1996), microbial community structure (Lin et al., 2019), and nutrition and water retention (Zang et al., 2005). Recognition of the benefits of retaining organic matter (OM) in soils is reflected in the increasingly broad interest in biochar development (Edmonson et al., 2015), its characteristics, and how it modifies soil health, nutrition, and water retention. Moreover, climate, land use change, and management all affect SC, often in different or unknown ways. The thermodynamically more resistant part of SC is commonly referred to as BC and has recently received a lot of attention (Schmidt, 2004), not only because of the contributions of industrialization (soot) but because of the increased inputs into ecosystems due to wildfires. BC is ubiquitous in soils, but its abundance is variable with estimated average values of 1%–6% of the total SOC, while some soils in Germany have been reported to contain 15%–45% (Schmidt et al., 2002) and even 60% in Canadian Chernozems (Ponomarenko

Core Ideas

- Using thermo-gravimetric analysis we quantify soil organic matter and inorganic carbon in a single measurement.
- In addition, we separate between readily decomposable organic carbon and resistant black carbon.
- Twenty five years of monitoring data show a consistent total carbon/loss on ignition ratio of 0.55 in British soils.
- Thermogravimetry is an excellent method for long time monitoring programs.

& Anderson, 2001). Distribution of BC in the landscape is not homogeneous with canopy trapping being identified as a mechanism to accumulate BC in soils under trees in urban areas (Beckett et al., 2000) and natural environments (Chew & Gallagher, 2018; Soares Goncanves Serafim et al., 2023). Moreover, methodologies to quantify BC are very expensive and time consuming, for example, concentrated nitric acid oxidation, elemental analysis after peroxidation and acidification, and C-NMR spectroscopy. A short review of the methods can be found in Forbes et al. (2006). Hence, the novel method presented provides a rapid and cost-effective way of differentiating the three important C pools. Potentially, monitoring changes in these pools will provide greater insight into changes in C with respect to management aims and ecosystem function outcomes.

Methods are required not only to differentiate SC pools but also to be robust, offer high precision, and be future proof on decadal to century-long time scales; small changes in soil stocks can then be reliably estimated. Soil scientists have used several methods over the years to measure SOM or SOC, but the needs of 2- to 3-year experiments are quite different to long-term monitoring over decades. Moreover, the methods used in scientific investigations may differ from those used in commercial laboratories, where the quality and cost balance may change depending on the end use. As a result, there are different measurement tools, often with multiple methods used for assessment. Here we focus on the suitability of tools and methods for long-term monitoring.

In this study, using standard materials and a large national monitoring soil data set ($n = 456$), we aim to (1) produce a new routine methodology that separates SOM, BC, and IC pools, all with different thermal stabilities and (2) quantify the errors associated with the determination of LOI using muffle furnace and TGA, and to determine the errors when measuring SOC using TC analyzer.
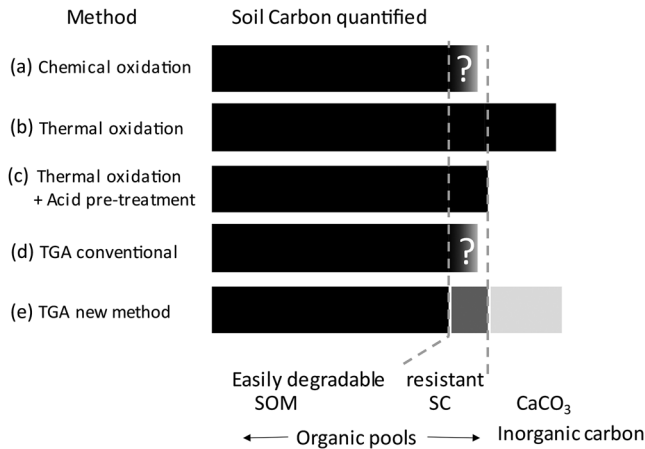
FIGURE 1 Description of the different carbon pools determined by (a) chemical oxidation, (b) thermal oxidation, (c) thermal oxidation after removing inorganic carbon, (d) thermo-gravimetric analysis (TGA) at 550°C for 6 h, and (e) TGA using method A in Table 1. SC, soil carbon; SOM, soil organic matter.

2 | MATERIALS AND METHODS

2.1 | Method development and review

SOM is measured using LOI by the weight difference of a sample before and after oxidizing OM at high temperatures (e.g., Ball, 1964; Nelson & Sommers, 1996). LOI has the advantage of using bigger aliquots of fine earth (5–10 g), it does not need any pre-treatment and has no toxic waste. However, it has been criticized for not being specific enough for scientific studies since there are other weight losses that occur when heating a soil at high temperatures. LOI was traditionally conducted in crucibles using a muffle furnace, and hence testing different times and temperatures to obtain the best methodology was time-consuming. Consequently, multiple time and temperature combinations resulted (Nelson & Sommers, 1996).

The LOI method is simple to perform; however, the lack of adoption of a unified method (temperature and time combination) hinders comparison of data across laboratories. The temperature chosen for the oxidation of organic molecules in the LOI method has been the focus of many discussions (Hoogsteen et al., 2015; Jensen et al., 2018; Pallasser et al., 2013). Two main aspects need to be taken into consideration: one is that molecules comprising SOM have very different thermodynamic stabilities (DeLapp & LeBoeuf, 2004) and the second is that the degradation processes are kinetic (Davidson & Janssens, 2006; LaRowe & Van Capellen, 2011). In other words, when oxidizing SOM, the temperature used and the period for which the sample is held at that temperature are critical to ensure total oxidation and hence quantification. An additional challenge is that some minerals in the soil may be transformed when heated at high temperatures: dehydration, dehydroxylation, and decomposition have been

observed and used as a way of studying clay minerals, especially in combination with X-ray analysis. This change in mineral structure usually occurs in clays, for example, kaolinites, halloysite, montmorillonite, and micas in the range of 450°C–650°C (e.g., Plante et al., 2009).

A survey of the literature reveals a variety of approaches taken by researchers to measure LOI. Ball (1964) used low temperatures for longer periods of time, 375°C for 16 h, Christensen and Malmros (1982) used mid-range temperatures with medium waiting times, 550°C for 4 h, and Spain et al. (1982) applied high temperatures with low periods of waiting time, 950°C for 0.5 h. Nelson and Sommers (1996) present a table with temperature and waiting times used in 14 different scientific papers, analyzing LOI in soils from Australia, North America, Israel, and Europe. Within those studies, 11 different temperatures and 14 different waiting times were used, indicating the lack of consistency across soil science. Salehi et al. (2011) more recently used the Schulte and Hopkins (1996) method to analyze the thermal mass loss (TML) of soils at 300°C, 360°C, 400°C, 500°C, and 550°C of 100 samples. They concluded that the optimum temperature to quantify SOM using the LOI methodology was "around 360°C." Therefore, there is a general agreement that using temperatures below 400°C is recommended to minimize dehydroxylation of clay and the waiting time to reach equilibrium should be between 8 and 16 h (Ben-Dor & Banin, 1989; Salehi et al., 2011). However, many published methods and most commercial laboratories still use 550°C for 3–4 h (Schlichting et al., 1995; Soil Survey Staff, 1996, Method 6A2a).

Modern automated TGA analyzers have a range of advantages over muffle furnace methods. They offer high throughput, minimize methodological errors, and are capable of measuring temperatures of 1000°C, enabling $CaCO_3$ determination. New TGA instruments can analyze a representative 5–10 g sample in a highly consistent and reproducible manner. Moreover, the introduction of automated TGA systems coupled with other detector systems like Fourier transform infrared (FTIR), gas chromatography, isotope-ratio mass spectrometry, and elemental analysis allows for the identification of the composition of the TML at different temperatures occurring during the oxidative process. In addition, the spectral aspect of the measurement means that investigations can be conducted to link particular temperature regions to specific soil components (Provenzano & Senesi, 1999; Schnitzer & Hoffman, 1965; Schnitzer et al., 1964; Shurygina et al., 1971). There is mounting evidence to show that most soils experience two TML peaks of interest, one in the range of 200°C–350°C and the other from 500°C to 600°C (Plante et al., 2009; Schnitzer et al., 1964; Turner & Schnitzer, 1962), with the two peaks associated with two organic fractions with different thermal stabilities (Schnitzer & Hoffmann, 1966).

Although the presence of different pools of SOM with different thermal stabilities has been recognized for a long time, it is only recently, with long-term monitoring and pressure

TABLE 1 Thermogravimetric methods A and B used in this study. LOI_{550} is the loss on ignition measured at 550°C, where LOI is loss on ignition.

Method	Temperature (°C)	Parameter measured	Ramp Rate (°C/min)	Hold time (h)	Total time (h)
A	25–105	Hygroscopic water	6	03:17	03:30
	105–375	LOI	6	15:00	15:45
	375–650	Black carbon + others	2	02:00	04:17
	650–1000	Calcite	6	03:00	03:58
B	25–105	Hygroscopic water	6	10:00	10:13
	105–550	LOI_{550}	6	05:00	06:14

to achieve multifunctional management outcomes, that the importance of separating SOM, BC, and $CaCO_3$ has come to the fore.

2.2 | Standards

We used pure substances of the most common soil minerals and plant components to investigate their oxidative behavior under increasing rates of heating: 2°C/min, 5°C/min, and 10°C/min, we also used methods A and B in Table 1 that includes a waiting period after each temperature increase. We selected cellulose (cellulose acetate phthalate, Sigma Aldrich), lignin (lignin alkali, Sigma Aldrich), kaolinite (natural, Sigma Aldrich), montmorillonite (K 10, Sigma Aldrich), charcoal (VWR International Ltd.), and a commercially available biochar (from www.woodtekbiochar.com,); the raw material used to produce biochar was entire tree biomass, pyrolysis temperature was 800°C for 10 min., and the TC was approximately 77%.

We used calcium oxalate hydrate as standard (Sigma-Aldrich) and four internal soil standards—Bangor standard 1 (BS1) and Bangor standard 3 (BS3) both Brown soils from North Wales, UK and SR3 and SR8 from Lancashire. X-ray analysis was performed on BS1 and BS3 to determine the clay mineral composition in the soils using a PAN analytical X'Pert Pro series diffractometer equipped with a cobalt target tube and an X'Celerator detector operated at 45 kV and 40 mA. We also analyzed the composition of the gasses emitted when heated between 375°C and 650°C for both standards BS1 and BS3 by using a TGA-FTIR (TGA 8000, PerkinElmer. IR: PerkinElmer Spectrum Two). IC was also measured in BS1 and BS3 using a FOG*L* digital soil calcimeter from BD inventions.

2.3 | Soils

The soil samples used in this study were collected in 2019 as part of the UK Countryside Survey (CS19) soil-monitoring

program. We measured the LOI of 456 soil samples from the top 0–15 cm, covering a wide range of habitats from across a national scale and representing soils from ~0%–100% LOI. The survey includes numerous other environmental metrics following the Countryside Survey protocols (Reynolds et al., 2013). Soil samples were air-dried, sieved through 2 mm, and quartered to obtain two subsamples of approximately 10 g. One soil subsample was placed in a crucible and measured by the crucible method and the other crucible was introduced into a LECO 700 thermogravimetric analyzer (TGA), in both cases we used method A in Table 1. All TGA runs were performed in an ambience of air and used laboratory air humidity (~50%) as starting point.

TC was measured in ball milled, oven dried (105°C for 3 h) soils using an Elementar Vario-EL elemental analyzer (Elementar Analysensysteme GmbH). Sample weights are usually 15 mg for peat and 15–60 mg for mineral soil samples (Emmett et al., 2010). This analysis was carried out using the UKAS accredited method SOP3102, at UKCEH Lancaster. Particle size distribution was measured using a Beckman Coulter LS13 320 laser diffraction particle size analyzer (Beckman Coulter Inc.) and following the methodology described in Lebron et al. (2020).

3 | RESULTS

Monitoring SOM change in soils requires strict quality control systems since SOM changes can be very small. For this purpose, four internal soil standards have been used since 1970. BS1, BS3, SR3, and SR8 are soils for which we have historic data for comparison purposes. The X-ray analysis showed that both BS1 and BS3 had mica as the dominant clay mineral in their composition. LOI measured with the traditional muffler method was no different on average from the data collected using TGA for the CS19 soils, average and standard deviation values for the muffler and TGA methods are shown in Table 2 for our soil standards. The results show that standard deviations were two to three times higher for the traditional muffler method (Table 2) compared to the TGA analyzer. Using soils

TABLE 2 Mean and standard deviation (SD) y covariance for the traditional muffler method, thermo-gravimetric analysis (TGA), and the thermal oxidation method (TC) using soil standards and calcium oxalate. The number of samples (N) analyzed was between 30 and 130. We used Method A from Table 1 for our loss on ignition (LOI) analysis.

Standard	N	Method	Metric	Mean (%)	SD	CV (%)
BS1	31	Muffler	LOI	12.53	1.13	9.01
BS3	31	Muffler	LOI	9.62	0.45	4.67
BS1	54	TGA	LOI	12.69	0.53	4.21
BS3	51	TGA	LOI	9.75	0.12	1.23
SR3	130	Thermal oxidation	TC	6.25	0.24	3.8
SR8	130	Thermal oxidation	TC	4.81	0.21	4.3
Calcium oxalate	27	Thermal oxidation	TC	15.9	0.179	1.13
Calcium oxalate	47	TGA	LOI	13.64	0.54	3.95

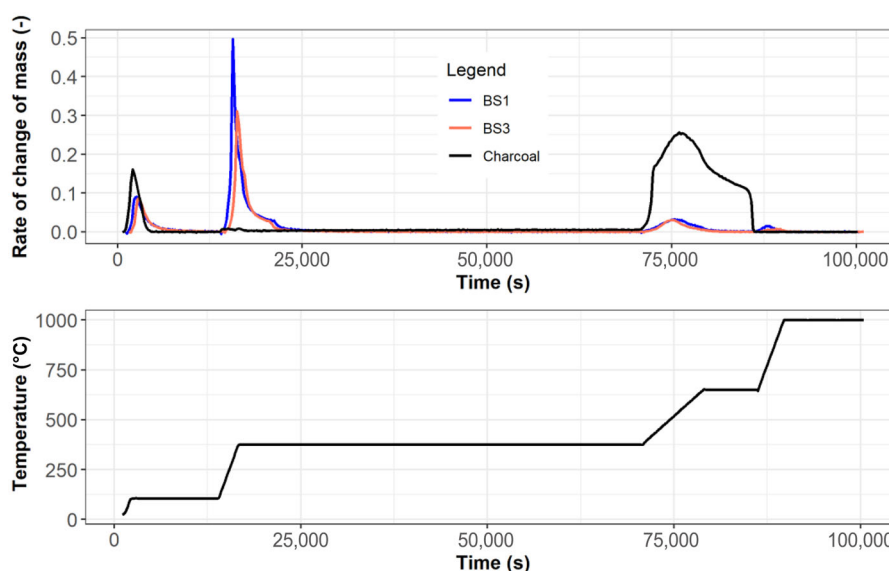Abbreviations: CV, coefficient of variation; BS, Bangor standard.

FIGURE 2 Thermal mass losses (TML) using thermogravimetric analysis (TGA) of Bangor standard 1 (BS1), Bangor standard 3 (BS3), and pure charcoal using Method A from Table 1.

as standards provides the combined errors of the instrument itself and the soil subsampling. To isolate the error coming from the instrument, we ran 27 samples of calcium oxalate, using thermal oxidation TC and 47 samples using the TGA. Table 2 shows that the TGA instrument has a higher coefficient of variation (3.96%) than the TC standard analyzer (1.13%). However, each gives comparable values for standard soils, most likely because the TGA, with the larger sample size, reduced sampling error compared to the TC analyzer.

The first derivative of the weight loss of the soil with increasing temperature indicates the rate of mass loss from the sample. A typical output thermogram from the TGA analyzer is presented in Figure 2 for BS1 and BS3 using method A described in Table 1. As temperature is increased, four main losses are observed for the standard soils. The first peak at 105°C belongs to the physically sorbed hygroscopic water, the peak at 375°C is the SOM, and the loss between 650°C and 1000°C is due to carbonates (Siewert, 2004) independently verified using a calcimeter (data not shown). The fourth peak, weight loss between 375°C and 650°C, was further investigated using a TGA-FTIR; we analyzed the gas emissions at that temperature interval to clarify whether those losses belonged to dihydroxylation of clay minerals or more resistant forms of C for our soil standards. The FTIR analysis showed no presence of H_2O, indicating that the micaceous nature of the clays in BS1 and BS3 did not contribute to the TML in the range of 375°C–650°C. FTIR also showed the presence of CO_2 indicating that the mass loss is due to thermodynamically more stable C compounds that did not burn in the 105°C–375°C interval.
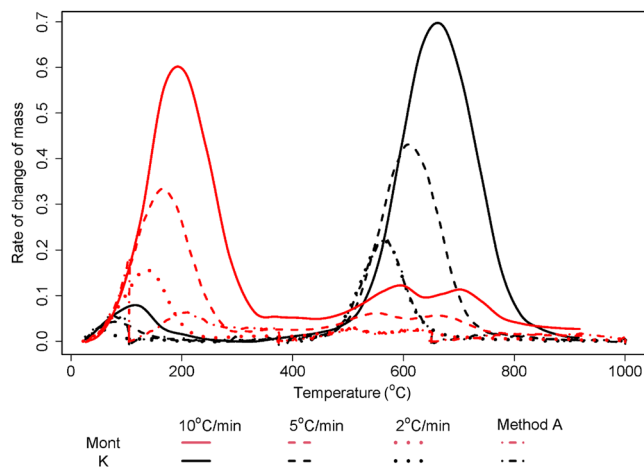
FIGURE 3 Thermal mass losses (TML) using thermogravimetric analysis for kaolinite (K) and montmorillonite (Mont) at 10°C/min, 5°C/min, 2°C/min, and 6°C/min with 16 h waiting times according to method A in Table 1.

Figure 2 also shows the TML for charcoal where we can observe that charcoal, one of the components of BC, is thermostable at 375°C and only decomposes in the 375°C–650°C interval. Thermograms for standard clay minerals 1:1 kaolinite and 2:1 montmorillonite were collected at 2°C/min, 5°C/min and 10°C/min and using method A in Table 1 (Figure 3). The figure clearly shows the importance of the rate and combustion time. Leaving for a longer time allows distinct peaks and thresholds to be observed. For example, the kaolinite and montmorillonite both show a complete loss of hygroscopic water at 105°C when left for 3 h. A rapid temperature ramp does not give sufficient time for the sample to dehydrate and, hence, a rounded peak occurs for kaolinite up to 200°C. Montmorillonite shows two peaks when the combustion is slowed (Method A): the 105°C water loss and the second loss maximum at about 200°C. Montmorillonite then shows no further weight loss when heated slowly. Conversely, kaolinite shows a distinct peak between 500°C and 600°C. The weight loss for pure montmorillonite at 200°C amounts to 0.5%, while the weight loss between 500°C and 600°C for kaolinite amounts to 8.3%. This indicates that unless montmorillonite is present in large quantities, it is unlikely to cause an error greater than 0.5% in SOM when using Method A. Kaolinite will only cause an error in SOM determination if the cutoff temperature chosen is above 450°C. The findings are consistent with the findings of Sun et al. (2009) for 15 reference materials, clays, and non-clay minerals.

Lignin and cellulose are the most common constituents in plants and hence important contributors to SOM. Standards of lignin (Figure 4A) and cellulose (Figure 4B) were run in our TGA at four different heating rates: 2°C/min, 5°C/min, and 10°C/ min and also using Method A (16 h) from Table 1. Figure 4 shows that rapid heating rates leads to large broad peaks with TML over a wider range of temperatures interfer-

ing and obscuring other TML from other forms of C. Slow combustion with a waiting time at 375°C ensures that all the material is oxidized. Hence, the determination of SOM will be consistent below a temperate of 375°C for 16 h. Conversely, charcoal does not begin to oxidize until temperatures above 400°C are reached (Figure 4C). Again, leaving sufficient time at 650°C enables all the charcoal to oxidize, meaning $CaCO_3$, which begins oxidizing at temperatures over 700°C, can be determined. Biochar (Figure 4D) was tested through interest as it is an increasingly common amendment in soils. These results indicate that this particular biochar behaves like SOM rather than charcoal and is fully oxidized below 375°C when allowed a waiting period of time. This may well change depending on the biochar and the processes and materials used to generate it.

In Figure 5, we present the soil thermograms for 465 soil samples from the monitoring program CS-2019. Analysis using method A clearly shows the soil weight loss falling into four regions, the first being the hygroscopic water; the second, the SOM below 375°C; the third, a small peak between 375°C and 650°C; and the fourth peak in the interval 650°C–100°C is the IC. The importance of leaving sufficient time is illustrated by the continuing oxidation for many samples as the temperature reaches 375°C. It is only after holding the temperature at 375°C for some time that oxidation is completed. The composition of the peak between 375°C and 650°C may contain some of the losses coming from mineral decomposition but since BC is ubiquitous in all soils, we can consider the peak between 375°C and 650°C to be a semiquantitative measure of BC in soils.

To further analyze our data, we grouped the soils from CS-2019 into six classes according to Hodgson (1997), this classification is based on SOM content—mineral soils (<6% of SOM; ~3.5% OC), organo-mineral (<22% SOM; ~12% OC), organic (>22% and <50% SOM; 12%–27.5% OC), peats (≥50% SOM; 27.5% OC)—we also included soils with distinct behavior like soils with carbonates (pH > 6.5) and a group of four soil samples (blue in Figures 6, 7, and 9) with unusual mineralogy. We investigated TML in the different temperature intervals and identified the soil classes with loss of weight in each interval (Figure 6). The weight loss between 375°C and 650°C was compared to TC measurements (Figure 6A). The results show distinct behavior of a few soils (blue markers) which were identified as a coal mine restored area. These soils had distinctly higher weight loss in this temperature range but tended to have low C contents, this weight loss is likely due to geological materials brought as part of the landscape restoration process rather than pedogenic minerals, in general there are 2%–3% weight losses for most soils in that interval. Increasing the temperature range from 650°C to 1000°C highlights the weight loss due to carbonate. In both the TC graph (Figure 6B) and pH graph (Figure 6C), soils with a pH > 6.5 are distinct and lose weight in this
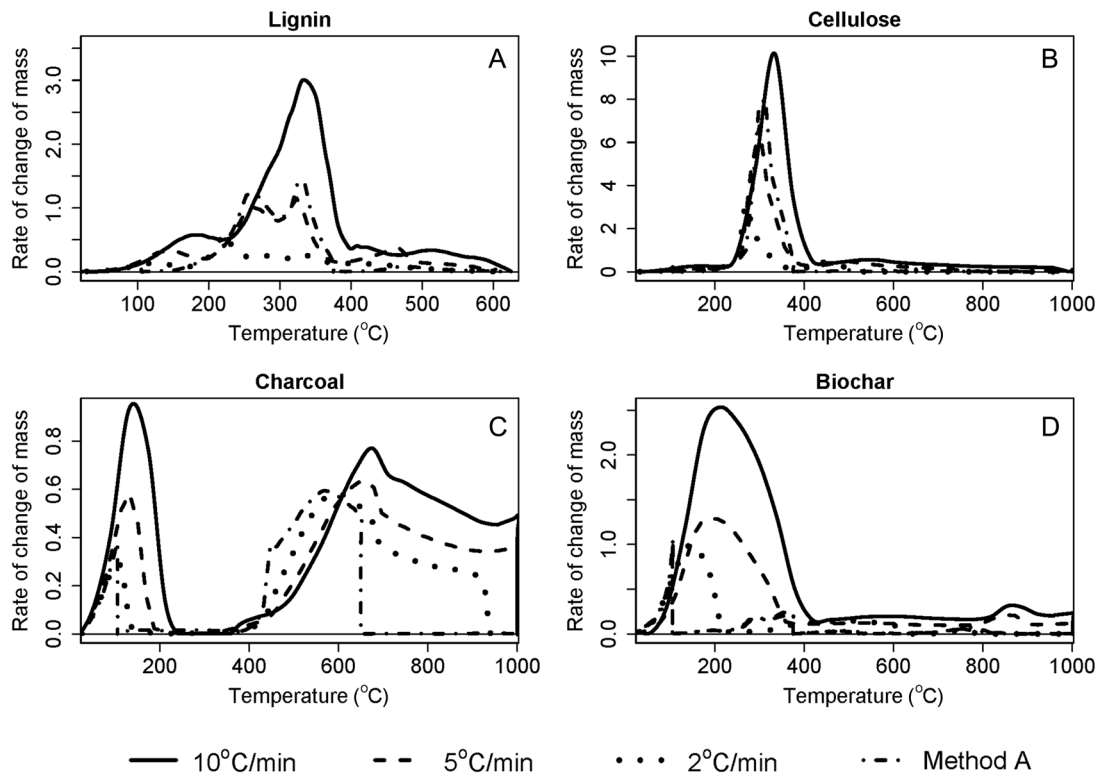
FIGURE 4 Thermal mass losses (TML) using thermogravimetric analysis for lignin (A), cellulose (B), charcoal (C), and biochar (D) at 10°C/min, 5°C/min, 2°C/min, and 6°C/min with 16 h waiting time according to Method A in Table 1.
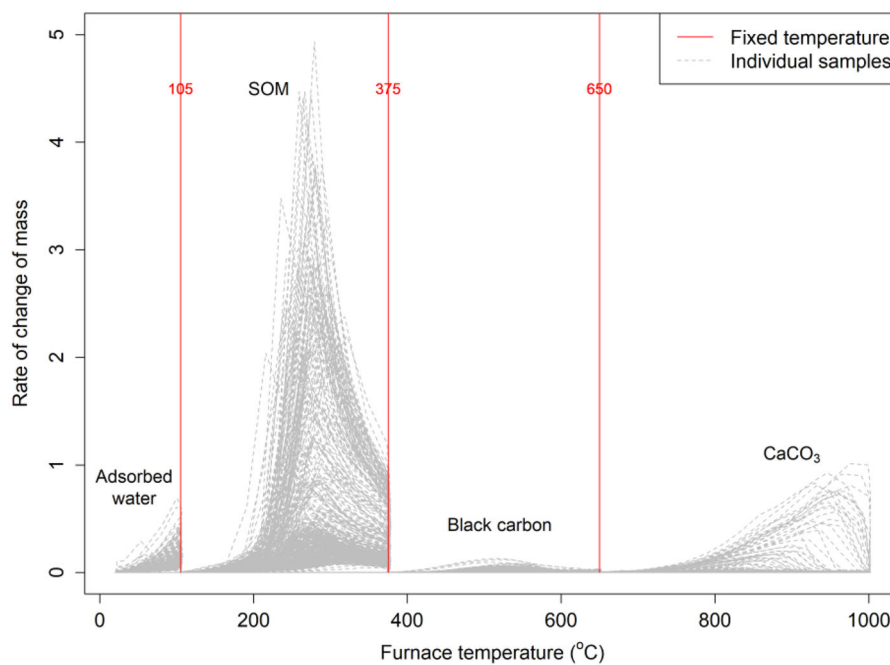

FIGURE 5 Thermal mass losses (TML) using thermogravimetric analysis for 460 soil samples from Countryside Survey for the year 2019 using Method A from Table 1. SOM, soil organic matter.
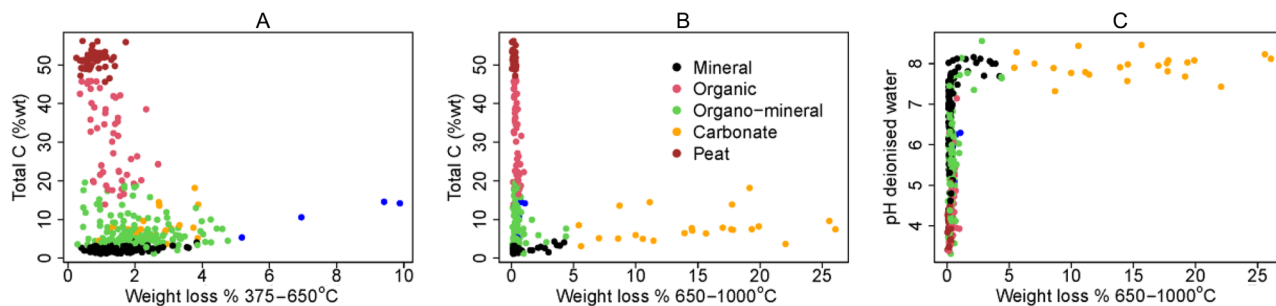
FIGURE 6 Soils thermal mass losses (TML) measured with the thermograms between 375°C and 650°C (A) and between 650°C and 1000°C (B) versus the total carbon of the sample measured with thermal oxidation. Plot C shows the TML between 650°C and 1000°C versus pH measured in deionized water. All soils were from the monitoring program CS19.
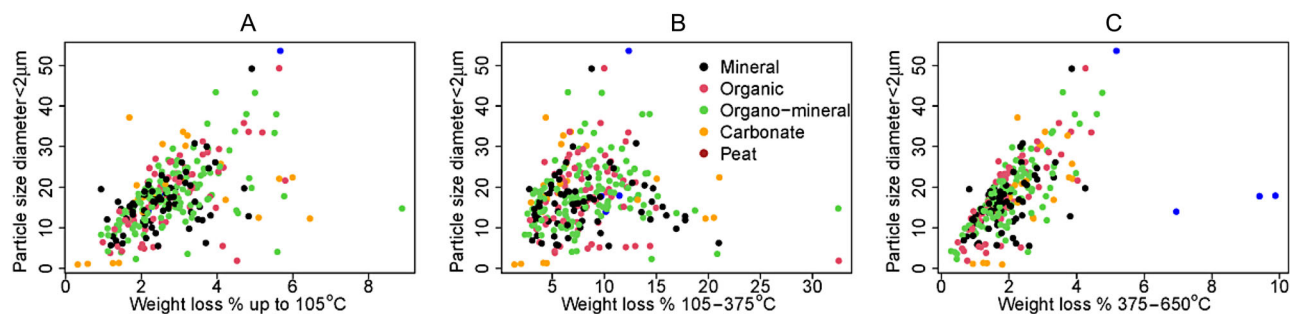

FIGURE 7 Relationship of thermal mass losses between 25°C and 105°C (A), 105°C and 375°C (B), and 375°C and 650°C (C) with clay content for soils from the monitoring program CS19.

temperature range due to the transformation of carbonates into CaO with the release of CO_2.

The contribution that the soil clay size components may make to the TML at each temperature interval is evaluated in Figure 7. At temperatures up to 105°C, the soils show a positive trend with increasing clay content. The clay influence disappears between 105°C and 375°C and re-emerges between 375°C and 650°C. This suggests that mineralogy is one contributing factor to mass loss between 25°C–105°C (hygroscopic water) and between 375°C and 650°C (possible contribution of clay mineral dihydroxylation and/or charcoal particles <2 μm). Silt content showed no trend in any of the temperature intervals for any of the soils (data not shown) and sand content showed the inverse relationship shown in Figure 7 for the three temperature intervals (data not shown).

The separation of the three C pools in soils allows us to visualize and analyze the distribution and changes with time of the more biochemically active pool of C (LOI) versus the less active ones (BC and IC). This is an important step since as to our knowledge, no one has developed a routine method for determining all three components of SC in a single measurement procedure. At present, the BC component is semiquantitative and provides an upper boundary for the levels of BC in the different habitats in the United Kingdom. Figure 8 shows the three TML classes associated with C pools

according to habitats in the United Kingdom. These indicate that wet acid environments have more C, as expected, but that BC is generally higher as a fraction in improved land. Carbonate is high in calcareous grasslands as expected and not found in the more acid environments.

The amount of C in SOM for UK soils shows a consistent and strong linear trend as shown in Figure 9. The linear regression for these data with the intercept set to zero gives a slope of 0.55 with an R^2 of 0.99. The same 0.55 ratio was found in previous Countryside Survey years 1978, 1998, and 2007 (Reynolds et al., 2013). Note that the carbonate and blue-marked samples in particular deviate somewhat from the regression line.

4 | DISCUSSION

SOM long-term monitoring requires an extraordinary level of method consistency, over decades, to provide the accuracy and reproducibility to detect changes, particularly as these changes may be very small. LOI determination using the new TGA analytical instruments has the advantage of being an automated, analyst independent measurement and is reproducible as shown in Table 2. However, the methodology must be clearly established if data from different laboratories are to be compared.
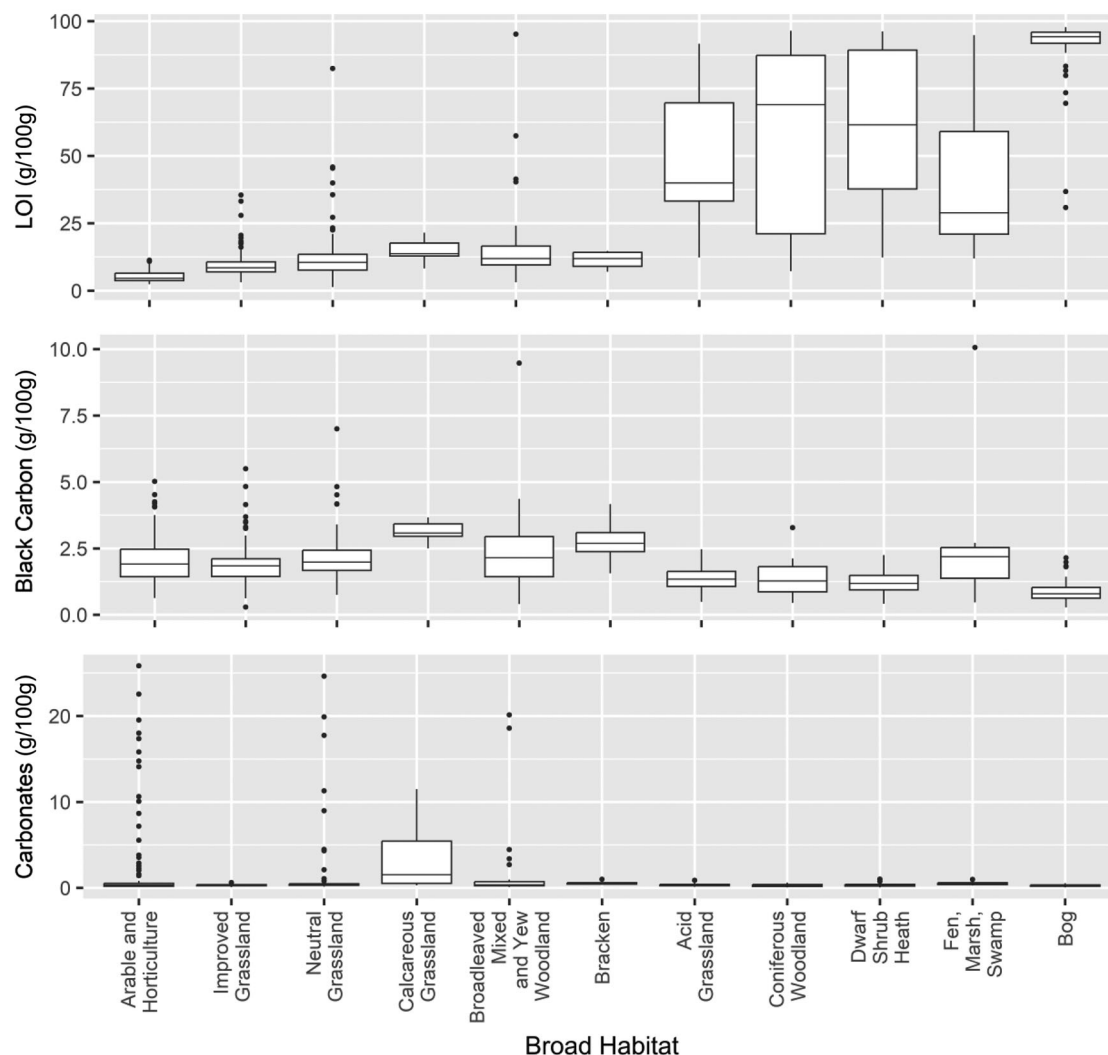
FIGURE 8 Loss on ignition (LOI) and thermal mass losses (TML) between 375°C and 650°C and inorganic carbon (IC) in the soils from Countryside Survey for the year 2019 according to habitats. TML 375°C–650°C is an estimation of the upper level of black carbon (BC) content.

Initial technical considerations, preferably before buying a machine or selecting a laboratory to perform the analysis, include (1) the amount of soil used to perform the analysis. Different machines have different material capacities, some TGA instruments have a limitation of up to 100 mg of sample and they may require ball-milling to provide a representative soil aliquot, not ideal for high throughput. A 10-g sample holder, like the one used in this study, permits the use of 2-mm sieved soil and allows for reproducibility; (2) the gas composition in which the reaction takes place; some instruments can accommodate an oxygen-enriched atmosphere in which the reaction rate is faster than in air. In this study, laboratory air was used with 21% oxygen composition.

The kinetic nature of the SOM thermo-degradation requires a clear definition of the oxidation process when analyzing for LOI. In other words, the temperature used and the rate at which the temperature is applied is critical as demonstrated in Figure 4, overlapping TML's can be obtained when the temperature or the rate is not appropriately chosen. For example, we found that LOI_{550} overestimates SOM by up to 15% in the case of BS3 (Table 2) when compared with 375°C (Method A) as shown in Table 3, this overestimation of SOM by the LOI_{550} method is due to the grouping of biochemically more reactive SOM with the more thermostable BC as demonstrated in Figure 5 and by our TGA-FTIR results. The differentiation of the two different thermostable pools of C in soils is critical if we want to improve our understanding CO_2 dynamics in soils (Edmondson et al., 2015). BC is a quasi-inert material with a limited role in the biogeochemical cycle, so separating it from SOM is advantageous for differentiating between soil health and climate change processes for example. Moreover, one of the objectives of SOM monitoring for soil health monitoring is to quantify changes, as it will be more relevant to exclude BC, which is likely to remain constant.

TABLE 3 Thermal mass losses (TML) expressed in percentage referred to oven dry weight (odwt) and standard deviations for Bangor standard soil 1 (BS1) and Bangor standard soil 3 (BS3) using method A and method B from Table 1.

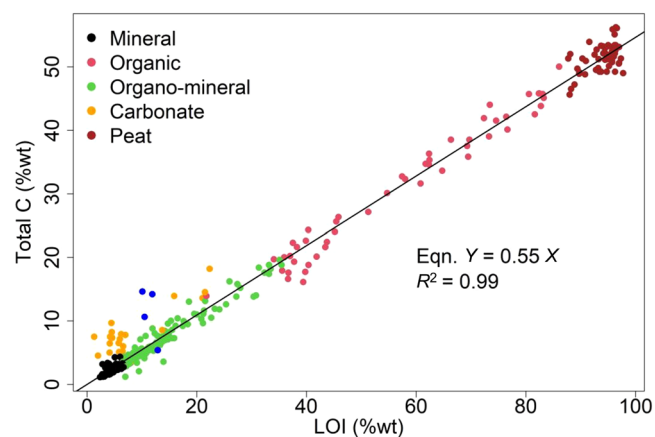| Method	Temperature (°C)	TML (% odwt)	
		BS1	BS3
A	25–105	3.51 ± 0.10	2.98 ± 0.08
	105–375	12.69 ± 0.53	9.75 ± 0.12
	375–650	2.97 ± 0.06	2.25 ± 0.04
	650–1000	1.33 ± 0.03	0.79 ± 0.03
B	25–105	3.53 ± 0.14	3.13 ± 0.06
	105–550	13.14 ± 0.39	11.26 ± 0.08

FIGURE 9 Relationship between total carbon (TC) obtained by thermal oxidation method and loss on ignition (LOI) using thermo-gravimetric analysis (TGA; weight loss percentage 105°C–3750°C). Color code according to main characteristics of organic carbon content and/or habitat.

Quantification of BC in soils is not trivial and there are very few data available for natural ecosystems. The ability to separate SOM from BC using method A provides a semiquantitative approach for the estimation of BC that might further be improved, for example, by using a TGA-FTIR. Although the TML between 375°C and 650°C is not exclusive for BC, it provides an upper bound for BC content in our soils; Figure 8 shows the TML between 375°C and 650°C for the different habitats in the United Kingdom together with LOI and IC for the 456 soils in CS2019.

Although SOM is an important parameter, many models require TC as an input, we found that the relationship between TC and LOI shown in Figure 9 has been consistent over the years for Great Britain (Reynolds et al., 2013) with a slope of 0.55. Other ratios for the TC/LOI relationship have been published by other laboratories for soils, for example, 0.58 when using 550°C (Jensen et al., 2018). However, the different slopes, in this case, are consistent with methodological differences due to woody materials being decomposed at 550°C.

Given the growing importance of C change measurements, standardizing SOM measurements at 375°C will reduce the uncertainty related to TML between 375°C and 550°C, which may be due to competing sources.

The consistency of the ratio TC/LOI = 0.55 for soils across decades for Countryside Survey is remarkable and points, perhaps, to an underlying decomposition convergence point. It is well known that the percentage of C in different organic compounds in soils is very different; it ranges from 90% to 80% for simple aliphatic and aromatic compounds to 20% for some amino acids (see Figure S1 for a range of examples). Sugars and cellulose are often reported ∼0.44 and Lignin ∼0.65; soft plant parts are reported as being ∼0.45 and woody ∼0.49 (Ma et al., 2018). The value of 0.55 for temperate soils lies midway between that for cellulose and lignin, perhaps suggesting the temperate Great Britain soil OM is a balance of similar materials. In comparison, Arctic soils with lots of fresh plant material and low decomposition rates have been found to have a slope of 0.46 (Weber, 2022). Conversely, as organic material is compressed and turns to coal, values as high as ∼0.89 are reported for anthracite. Returning to the soil humic and fulvic acids are more in the 0.4–0.6 range, the formulae for these complex compounds are variable, with the very existence of such compounds being recently questioned (Burdon, 2001; Piccolo, 2001; Sutton & Sposito, 2005). Sutton and Sposito (2005) and Swift (1999) proposed that humic substances are collections of diverse, relatively low molecular mass components forming dynamic associations. Considering the amount of controversy and complexity surrounding SOM, the fact that we obtain a consistent relationship between TC and LOI is remarkable. Figure 9 shows that whatever processes occur in the soil, there is a commonality among soils that produces the same average C ratio for SOM regardless of habitat type, vegetation, land use, or management. Further exploration of this general pattern may help us to find unifying principles in soil biogeochemistry that will allow us to move forward in our modeling of SOM.

5 | CONCLUSIONS

There is a need to standardize SC measurement methodologies to provide a consistent database for monitoring soil health and its change. Consistent, robust measurements are provided using a temperature of 375°C for 16 h that differentiates between SOM and BC or dehydroxylating clay minerals. Measurements of LOI on soil standards indicate that TGA achieves double the precision of a muffler furnace and is similar to TC analyzer measurements on soils. The novel method proposed in this work provides determination of OM and IC, separating the OM into the more biochemically active SOM and the more resistant BC in a single measurement. The method proposed in this study had a consistent

ratio for TC/LOI = 0.55, not only among soil types and land uses for Great Britain but also in time. We acknowledge that this ratio may change depending on decomposition and global region. However, the low cost, large sample size, robustness through time, and measurement of SOM and carbonate make LOI, using TGA, an important tool for long-term monitoring applications using the proposed temperature and time regime.

AUTHOR CONTRIBUTIONS

Inmaculada Lebron: Conceptualization; data curation; formal analysis; investigation; methodology; writing—original draft; writing—review and editing. **David M. Cooper**: Software; visualization; writing—review and editing. **Michele A. Brentegani**: Formal analysis; validation. **Laura A. Bentley**: Data curation; visualization. **Gloria Dos Santos Pereira**: Formal analysis; writing—review and editing. **Patrick Keenan**: Formal analysis. **Jack Bernard Cosby**: Funding acquisition; project administration; resources. **Bridget Emmet**: Funding acquisition; methodology; resources. **David A. Robinson**: Conceptualization; investigation; methodology; writing—original draft; writing—review and editing.

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