Contribution of organic amendments to soil organic matter detected by thermogravimetry

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Abstract

Sustainable soil management requires reliable and accurate monitoring of changes in soil organic matter (SOM). However, despite the development of improved analytical techniques during the last decades, there are still limits in the detection of small changes in soil organic carbon content and SOM composition. This study focused on the detection of such changes under laboratory conditions by adding different organic amendments to soils. The model experiments consisted of artificially mixing soil samples from non-fertilized plots of three German long-term agricultural experiments in Bad Lauchstädt (silty loam), Grossbeeren (silty sand), and Müncheberg (loamy sand) with straw, farmyard manure, sheep faeces, and charcoal in quantities from 3 to 180 t ha^{-1} each. In these mixtures we determined the organic carbon contents by elemental analysis and by thermal mass losses (TML) determined by thermogravimetry. The results confirmed the higher reliability of elemental analysis compared to TML for organic carbon content determination. The sensitivity of both methods was not sufficient to detect the changes in organic carbon content caused by small quantities of organic amendments (3 t ha^{-1} or 0.1–0.4 g C kg^{-1} soil). In the case of elemental analysis, the detectability of changes in carbon content increased with quantities of added amendments, but the method could not distinguish different types of organic amendments. On the contrary, the based on analysis of degradation temperatures, the TML allowed this discrimination together with their quantitative analysis. For example, added charcoal was not visible in TML from 320 to 330°C, which is used for carbon content determination. However, increasing quantities of charcoal were reflected in a higher TML around 520°C. Furthermore, differences between measured (with $TML_{110–550}$) and predicted mass loss on ignition using both organic carbon (with TML_{330}) and clay contents (with TML_{140}) were confirmed as a suitable indicator for detection of organic amendments in different types of soils. We conclude that thermogravimetry enables the sensitive detection of organic fertilizers and organic amendments in soils under arable land use.

Key words: elemental analysis / fingerprinting / model experiments / soil organic carbon / thermal decay dynamics

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1 Introduction

Soil organic matter (SOM) is defined as a complex mixture of organic carbon in living organisms and of compounds in various stages of decomposition (*Trumbore*, 1997; *Brady* and *Weil*, 2008). SOM influences the physical, chemical and biological properties of soils, and SOM persistence determines ecosystem properties (*Schmidt* et al., 2011; *Gregorich* et al., 2015). The dynamics of SOM have significant importance for global carbon cycle (*Field* et al., 2007; *Conant* et al., 2011; *Dignac* et al., 2017) and SOM is recognized as key parameter to the sustainability of land use (*Doran*, 2002; *Scheffer* et al., 2010; *Kleber* and *Lehmann*, 2015). In agricultural soils, fertilizers and organic amendments, *e.g.*, straw, farmyard man-

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ure, and slurry manure, are frequently incorporated in soils to increase the SOM content. In addition, these fertilizers are subjected to alteration over time through decomposition related to microbial immobilization and mineralization (*Liu* et al., 2006). These processes improve soil quality and nutrient availability for the plants, thus leading to improved crop yields (*Haynes* and *Naidu*, 1998; *Körschens* et al., 2013).

However, the influence of organic fertilizers and amendments on soil properties and soil functions can only be quantified to limited extend (*Gray* et al., 2011; *Dignac* et al., 2017). It seems difficult even to capture changes in organic carbon contents (*Haynes* and *Naidu*, 1998; *Fontaine* et al., 2003; *Ferreras* et al., 2006; *Kätterer* et al., 2014) under the influence of soil microorganisms, interaction with mineral soil components, differing climatic conditions, or soil management practices.

The most popular tool for "assessing" SOM is the determination of the soil organic carbon (SOC) content (*Haynes*, 2005). Typical SOC quantifications are based on titrations, while other use gravimetric, volumetric, spectrophotometric, or chromatographic methods (*Schumacher*, 2002). Widely applied methods (*Jandl* et al., 2014) are Walkley–Black method (wet oxidation of organic carbon) (*Walkley* and *Black*, 1934), loss on ignition (LOI; determination of weight percent organic matter), and dry combustion by elemental analysis (EA) with CO_2 detection (*Dean Jr.*, 1974; *Nelson* and *Sommers*, 1982). The Walkley–Black method is labor intensive and may lead to incomplete oxidation of organic carbon (*Nelson* and *Sommers*, 1996). LOI is a simple approach (*Wang* et al., 2012; *Pallasser* et al., 2013), but is characterized by limited accuracy (*Wang* et al., 2013; *Ghabbour* et al., 2014; *Hoogsteen* et al., 2015). SOC determination by EA is attractive due to its reliability, accuracy, and relative low cost (*Pallasser* et al., 2013). Therefore, SOC content determination by EA is in use as the most applied reference method (*ISO*, 1996) in laboratories with high sample throughput.

The SOC content determination by EA is influenced by sampling methods as well as by the analytical accuracy. In literature the overall detection limit is described with standard errors of around 1 g C kg^{-1} soil (*Schumacher*, 2002), whereas the analytical accuracy of this method is much better (0.1 g C kg^{-1} soil). Similar conclusions were reached by *Körschens* (2010) and *Gattinger* et al. (2012) including the influence of soil sampling and other factors and implying higher analytical accuracy. As a result, monitoring small changes in SOC content due to management change, for example, is still a challenging task as the background SOC stock is large (*Jandl* et al., 2014) and the level of SOC content remains difficult to assess (*Wessolek* et al., 2008).

Traditionally, organic matter content is determined *via* LOI (*Dean Jr.*, 1974). It is based on the annealing of already oven dried samples in the muffle furnace at 550°C for several hours. Thermogravimetry (TG) extends this procedure with modern thermobalances to continuously record mass losses during soil heating (Mass Losses on Ignition–MLI) (*Oudghiri* et al., 2014; *Peikert* et al., 2015; *Kristl* et al., 2016). Together with standardization of sample preparation and new evaluation algorithms, it allows determination of organic carbon, total organic nitrogen, clay, and carbonates with high accuracy (*Siewert*, 2004). For example, SOC can be calculated using thermal mass loss (TML) between 320 and 330°C mentioned here as $TML_{320–330}$. The content of organic nitrogen can be calculated using $TML_{400–410}$ or $TML_{320–330}$ as well, whereas for clay content determination close correlation to results of the standard pipette method were observed for $TML_{120–130}$ and $TML_{520–530}$ if the water content of air dried soil samples was equilibrated (*Siewert* and *Kučerík*, 2015).

Correlations between $TML_{120–130}$ and $TML_{520–530}$ were found to be predictive for the indirect detection of extraneous organic carbon (*e.g.*, charcoal, ashes, cinder, *etc*.) in soils, because this composition of organic matter causes increased mass losses in higher temperature ranges as compared to "native" SOM (*Siewert* and *Kučerík*, 2015). Furthermore, TML used for SOC and clay content determinations correlate with MLI used for SOM content determination (*Wang* et al., 2013; *Ghabbour* et al., 2014; *Hoogsteen* et al., 2015). The transformed equation SOC = 0.48 × total organic matter – 0.12 × clay + 0.2 (*Kučerík* et al., 2016) was found to be similar to other authors (*Konen* et al., 2002; *de Vos* et al., 2005; *Wright* et al., 2008) meaning broader applicability to different types of soils. These specifics of TG suggest the practical applicability for detection of changes in SOM considering interactions between soil components and providing information important for agricultural practice.

Therefore, this work aimed to investigate the detection opportunities for changes in the amount of SOM by thermogravimetry compared to elemental analysis and to determine the contribution of organic amendments to soil organic matter by using thermal decay dynamics.

2 Material and methods

Model experiments consisted of artificially increasing the organic carbon content by adding various quantities of different types of organic amendments under laboratory conditions with subsequent analyses of mixtures with both EA and TG methods. We used different non-fertilized soils from long-term agricultural field experiments (LTAEs) to reduce unknown impacts of fertilizers.

2.1 Soil samples and organic amendments

The soil samples were taken from the Ap-horizon (25 cm depth) from three LTAEs in Germany with varying clay and carbon contents. They were located in Müncheberg (Brandenburg, Leibniz Centre for Agricultural Landscape Research, Nutrition Increase Experiment, established 1963), Grossbeeren (Brandenburg, Leibniz Institute of Vegetable and Ornamental Crops, Static Fertilization Experiment, established 1989), and Bad Lauchstädt (Saxony-Anhalt, Centre for Environmental Research, Static Fertilization Experiment, established 1902). Detailed description of the experiments were given by *Barkusky* (2009), *Rühlmann* (2009), and *Körschens* and *Pfefferkorn* (1998). Information of the soil types and characteristics are provided below:

(1) Müncheberg, Albic-Luvisol (WRB), 50 g kg^{-1} clay (loamy sand),
(2) Grossbeeren, Arenic-Luvisol (WRB), 55 g kg^{-1} clay (silty sand),
(3) Bad Lauchstädt, Haplic-Chernozem (WRB), 210 g kg^{-1} clay (silty loam).

The SOC contents (non-fertilized soils) were 5, 8, and 16 g C kg^{-1} soil in Müncheberg, Grossbeeren, and Bad Lauchstädt, respectively.

The samples of each LTAE were mixed with straw, farmyard manure, sheep faeces, and charcoal, as examples of frequently applied agricultural amendments. They represent easily degradable plant residues (straw), classical organic fertilizers (farmyard manure and sheep faeces), and an example of black carbon application for soil property improvement (charcoal).

The added quantities of organic amendments (Tab. 1) representing (a) low rate for expected detection limit for changes in carbon content (0.1–0.4 g C kg^{-1}, or 3 t ha^{-1} of organic amendments), (b) typical application rates in agricultural practice (0.4–2.5 g C kg^{-1} or 20 t ha^{-1}), and (c) the highest fertilization rates in long-term agriculture field experiments (1.3–7.5 g C kg^{-1}, or 60 t ha^{-1}, *Körschens* et al., 2013). In order to consider the high differences in the content of dry mass in applied amendments (Tab. 1), farmyard manure and sheep faeces were added in additional extreme rates (3.8–5.0 g C kg^{-1} or 180 t ha^{-1} of organic amendments) in order to increase the comparability of added with straw and charcoal quantity of organic carbon. All of the artificial mixtures consisted of 10 g soil with the organic amendment in the amount equivalent from 3 t ha^{-1} to 180 t ha^{-1}.

2.2 Sample preparation and analysis

After sampling with an auger, all soil samples were gently air dried and passed to a 2-mm sieve. In order to create comparable content of bound water, the air-dried samples were exposed to a relative air humidity of 76% (at 22°C) for at least 2 weeks in desiccators. This conditioning exclude biodegradation at soil water content as close as possible to dry soils in field conditions (*Siewert*, 2001). The organic amendments were ground to 0.2 mm particle size (Retsch Ultra Centrifugal Mill ZM 200) after air-drying and, like the soil samples, stored at 76% relative humidity. After adding organic amendments into soils, the mixtures were immediately shaken for 2 h in an airtight glass container at room temperature (22°C), and prior to thermogravimetric analyses again conditioned at 76% relative air humidity for 2 weeks (Fig. 1).The analyses of organic carbon content of all samples were carried out in duplicate by dry combustion with a LECO TruMac CN analyser at a certified laboratory of LKS mbH in Niederwiesa (Germany) using standard procedures (*ISO*, 1996).

A thermoscale (Mettler-Toledo TGA/SDTA 851e) was used for the TG measurements. The measurement conditions were

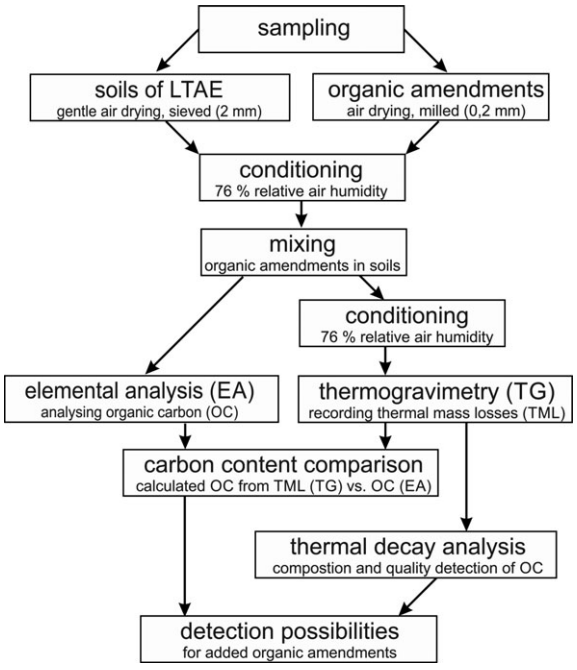

Figure 1: Scheme of experimental procedure of model experiments with artificial increase of soil carbon content by organic amendments, LTAE—Long-term agricultural field experiment.

Table 1: Basic properties of added straw (ST), farmyard manure (FYM), sheep faces (SF), and charcoal (CC) and expected changes in carbon content by adding different quantities of organic amendments.[a]

Type of organic Amendments		**ST**	**FYM**	**SF**	**CC**
Dry matter content (%)		86	23	35	80
Carbon content in dry mass (g kg^{-1})		402	413	357	706
Added quantity of organic amendments (fresh matter)	**(t ha^{-1} OA)**	**predicted increase in carbon content (g C kg^{-1} soil)**			
Low rate (expected detection limit)	3	+0.2	+0.1	+0.1	+0.4
Typical rate in practice	20	+1.5	+0.4	+0.6	+2.5
Highest rate in field experiments	60	+4.6	+1.3	+1.7	+7.5
Extreme rate for comparability	180	N/A	+3.8	+5.0	N/A

[a]OA: Organic amendments, N/A: Not analyzed.

as follows: heating 0.8 g–1.0 g of sample mass from 25 to 950°C with heating rate of 5°C min^{-1} and data acquisition of 1 reading per 4 seconds (one value per 0.3°C temperature increase). During the analytical procedure, the furnace with the sample was purged with a stream of air enriched by 76% relative humidity at 22°C with a flow rate of ≈ 200 mL min^{-1} (*Siewert*, 2004). TG analyses were carried out mostly in four replicates.

2.3 Data evaluation and statistical analysis

The evaluation of results started with the reduction of data to the means of thermal mass losses in 10°C temperature intervals. The resulting data are abbreviated here as TML (thermal mass losses) with given lower and upper temperature limit. For example, $TML_{320–330}$ describes TML from 320°C to 330°C. During the next step of evaluation, the organic carbon contents were calculated from TML proposed by *Siewert* (2004) for soil property determination, with selected equation for $TML_{320–330}$ because of the highest reliability and accuracy of this method.

The statistical analyses of changes in organic carbon content were carried out as multifactorial ANOVA with consideration of three soil types (corresponding to sites of LTAE, factor A), four types of organic amendments (factor B), three or four quantities of added organic amendments (factor C), and both TG and EA methods for carbon content determination (factor D). A similar procedure was applied to the dynamics of TML in 10°C temperature increase steps for organic carbon determination without factor D. For the comparison of selected means from main and combination effects the Tukey-HSD-test was applied.

All statistical analyses were carried out using STATISTICA® software (version 12.0) or Microsoft Excel® (2013). All tests were repeatedly carried out in R-statistics for validation of results.

3 Results and discussion

3.1 Organic carbon content determination

TG method showed significantly lower ($p < 0.05$; Tab. 2) organic carbon contents for non-fertilized initial soil samples than the EA method (Tab. 2). In natural soils a better comparability of both methods was found (*Siewert*, 2001; 2004). We hypothesized, that TG preferentially detects biologically transformed organic carbon, whereas elemental analysis detect the total carbon content. After adding low quantities (3 t ha^{-1}) of organic amendments both TG and EA methods did not display significant changes in organic carbon contents according to the accuracy limits of both methods as described in *Schumacher* (2002) for EA and *Siewert* (2004) for TG (Tab. 2).

With increasing quantities of added charcoal, the results of TG deviated to a larger extent from predicted values (*i.e.*, without charcoal) and from EA results ($p < 0.001$). Straw in contrast, caused an overestimation of carbon content in some samples by TG ($p < 0.001$), whereas in the case of farmyard manure and sheep faeces the carbon content determined by TG did not show deviations from predicted results and from results of EA.

Figure 2 presents differences in organic carbon content between soil mixtures and non-fertilized soils in order to simplify demonstration of changes in organic carbon content by reducing the influence of different soil types. This makes the under- and overestimation of the carbon content of charcoal and straw by TG more visible. These effects were similar in all three soil types (LTAEs, sites) for all quantities and types of organic amendments ($p < 0.001$; Tab. 3). The only exclu-

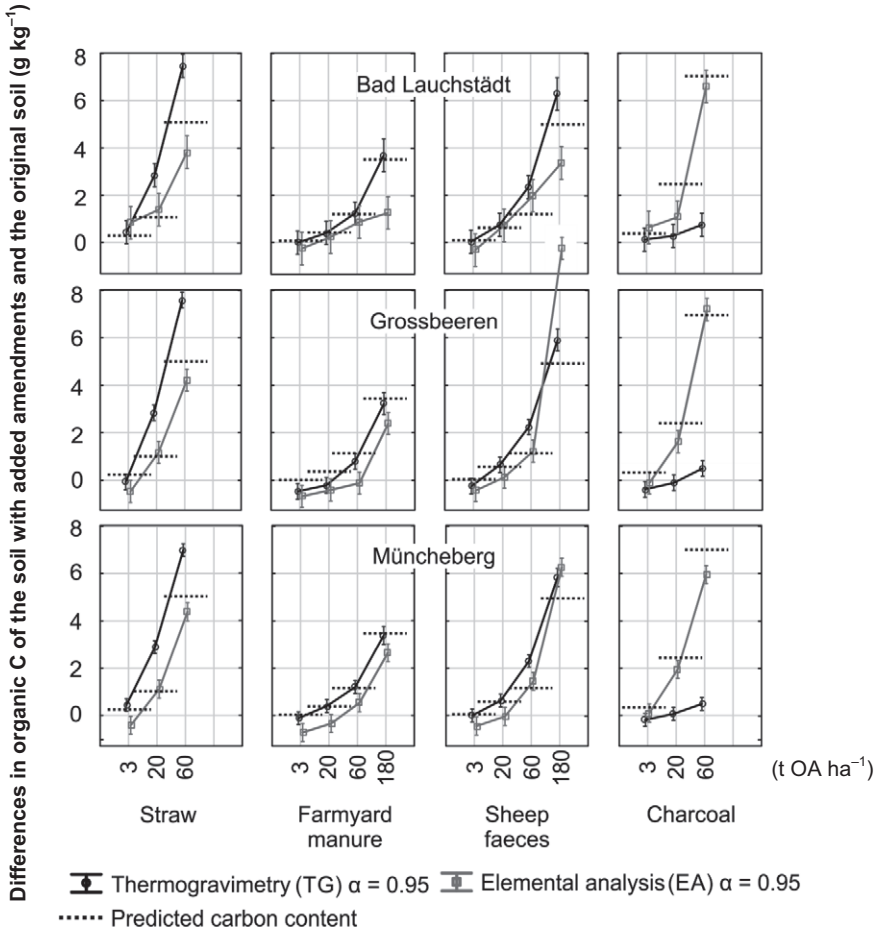

Figure 2: Changes in organic carbon (C) content by adding organic amendments (OA) to soils from different long term field experiments measured with EA and TG, presented as differences of measured organic C content of the soils with added OA minus the original soil (non-fertilized soil). Error bars indicate ± standard error of the means.

Table 2: Organic carbon content (g kg^{-1}) in mixtures of soils with organic amendments straw (ST), farmyard manure (FYM), sheep faces (SF), and charcoal (CC) in different quantities determined with elemental analyses (EA) and thermogravimetry (TG, based on $TML_{320–330}$). Numbers in parentheses are standard deviation.[a]

Site / soil:	Müncheberg (loamy sand, 50 g kg^{-1} clay)				Grossbeeren (silty sand, 55 g kg^{-1} clay)				Bad Lauchstädt (silty loam, 210 g kg^{-1} clay)			
Method	**Non-fertilized soil**											
EA	5.0 (0.2)				8.0 (0.1)				16.1 (0.2)			
TG	2.8 (0.0)				6.0 (0.1)				15.6 (0.0)			
	Organic amendments											
	ST	***FYM***	***SF***	***CC***	***ST***	***FYM***	***SF***	***CC***	***ST***	***FYM***	***SF***	***CC***
	+ 3 t ha^{-1} added											
EA	4.7 (0.0)	4.4 (0.1)	4.7 (0.2)	5.3 (0.2)	7.4 (0.1)	7.2 (0.2)	7.5 (0.2)	7.8 (0.2)	17.0 (0.4)	16.0 (0.2)	15.9 (0.1)	16.8 (0.2)
TG	3.2 (0.1)	2.7 (0.0)	2.8 (0.1)	2.6 (0.1)	6.0 (0.1)	5.6 (0.2)	5.8 (0.1)	5.7 (0.2)	16.0 (0.1)	15.5 (0.1)	15.6 (0.3)	15.7 (0.2)
	+ 20 t ha^{-1} added											
EA	6.3 (0.1)	4.8 (0.1)	5.1 (0.6)	7.1 (0.1)	9.1 (0.6)	7.5 (0.5)	8.0 (0.2)	9.5 (0.4)	17.6 (0.4)	16.4 (0.4)	17.0 (0.2)	17.3 (0.5)
TG	5.7 (0.3)	3.1 (0.2)	3.4 (0.0)	2.8 (0.1)	8.9 (0.6)	5.9 (0.1)	6.7 (0.2)	6.0 (0.2)	18.4 (0.6)	16.0 (0.2)	16.3 (0.1)	15.8 (0.2)
	+ 60 t ha^{-1} added											
EA	9.5 (0.0)	5.7 (0.6)	6.6 (0.1)	11.1 (0.2)	12.1 (0.4)	7.8 (0.4)	9.1 (0.6)	15.1 (0.8)	20.0 (0.6)	17.1 (0.2)	18.2 (0.4)	22.8 (0.5)
TG	9.8 (0.8)	4.0 (0.2)	5.1 (0.2)	3.3 (0.1)	13.7 (0.7)	6.9 (0.1)	8.3 (0.2)	6.6 (0.2)	23.0 (1.6)	16.8 (0.2)	17.9 (0.5)	16.3 (0.1)
	+ 180 t ha^{-1} added											
EA	N/A	7.8 (0.1)	11.4 (0.4)	N/A	N/A	10.3 (0.1)	17.6 (0.2)	N/A	N/A	17.4 (0.2)	19.6 (0.2)	N/A
TG	N/A	6.2 (0.3)	8.6 (0.2)	N/A	N/A	9.3 (0.2)	12.0 (0.0)	N/A	N/A	19.2 (0.1)	21.8 (0.6)	N/A

[a]N/A: Not analyzed.

sion is related to application of extreme rates of sheep faeces which leads to overestimation of results ($p < 0.01$) by TG (Bad Lauchstädt and Grossbeeren).

Summarizing these results, TG seems to have a limited ability to capture changes in organic carbon in soils containing organic amendments. The limited applicability of TG to soil organic carbon, however, is a known phenomenon. Deviations between EA and TG are described in *Siewert* (2004) as a possible consequence of extraneous carbon, which has not undergone stabilization processes as a part of biological regulation during soil formation. This effect may be reduced by biological transformation during digestion and composting.

Siewert (2004) and *Kučerík* et al. (2013) found increasing limitations in soil property determination *via* TML in dependency on quantity and quality of added organic carbon from anthropogenic materials (such as charcoal, ashes, cinder, *etc*.). Furthermore the level of transformation of organic amendments into SOM through storage, digestion, composting, *etc*., should be considered. This limits the applicability of TG for soil property determination. Nevertheless, it offers new opportunities for diagnostics of anthropogenic influences by analyzing of thermal decay profiles of individual organic amendments.

3.2 Thermal decay dynamics for the detection of different organic amendments

Figure 3 compares the dynamics of thermal mass losses for soils from Bad Lauchstädt, Grossbeeren, and Müncheberg before and after adding the highest rates of added organic amendments (60 t ha^{-1} of straw and charcoal, 180 t ha^{-1} of farmyard manure and sheep faeces). It reveals the soil influence on dynamics of thermal decay and their changes by added organic amendments. In all soil types (LTAEs, sites) a similar general trend was observed. Most changes have been observed between 200°C and 550°C, *i.e*., in temperature

Table 3: Multifactorial ANOVA (1) of organic carbon content in non-fertilized soils and (2) of changes in organic carbon content in mixtures of soils (A, Bad Lauchstädt, Müncheberg and Grossbeeren) with different types of organic amendments (B, straw, farmyard manure, sheep faeces, charcoal) and different quantities (C, 3, 20, 60 t ha^{-1}) presented as differences of measured carbon content in mixtures minus carbon content in non-fertilized soils with elemental analysis and thermogravimetry (D).[a]

(1) Determination of organic carbon content in non-fertilized soils			
Interaction factors	D.F.	F	*p*
Soil (A)	2	1469.6	0.000***
Method (D)	1	67.2	0.000***
Soil × method (A × D)	2	7.3	0.025*
(2) Detection of changes in organic carbon content in mixtures of soils with organic amendments			
Interaction factors	D.F.	F	*p*
Soil (A)	2	12.4	0.000***
Organic amendments (B)	3	389.5	0.000***
Quantity (C)	2	1127.7	0.000***
Method (D)	1	0.1	0.814
Soil × organic amendments (A × B)	6	1.3	0.251
Soil × quantity (A × C)	4	1.6	0.182
Organic amendments × quantity (B × C)	6	110.5	0.000***
Soil × method (A × D)	2	1.3	0.280
Organic amendments × method (B × D)	3	281.9	0.000***
Quantity × method (C × D)	2	11.1	0.000***
Soil × organic amendments × quantity (A × B × C)	12	2.1	0.018*
Soil × organic amendments × method (A × B × D)	6	1.2	0.328
Soil × quantity ×method (A × C × D)	4	0.6	0.677
Organic amendments × quantity × method (B × C × D)	6	99.4	0.000***
Soil × organic amendments × quantity × method (A × B × C × D)	12	2.0	0.027*

[a]The table gives the degree of freedom (D.F.), the variance ratio (F) and the probability level (*$p < 0.05$, ***$p < 0.001$) to assess organic carbon content depending on soil, organic amendment, quantity, and method of the model experiment data set. Note that the multifactorial ANOVA analysis was also carried out for the absolute values of organic carbon content determination in soil mixtures, but in order to point out the changes in organic carbon content independently from method (D) and soil (A) we present only the statistical analysis of the differences in organic carbon content between mixtures and non-fertilized soils.

areas of thermal decay of organic matter, a portion of which is also used for carbon content determination ($TML_{320–330}$; *Siewert*, 2004). The position and intensity of the thermal decay peaks depended on the type of added organic amendments. For example, addition of straw or sheep faeces mainly resulted in changing mass losses around 300°C with a peak for sheep faeces at 280°C and for straw at 310°C. In contrast, charcoal application caused the highest increase of mass losses at higher temperature around 500°C, whereas farmyard manure degraded continuously in a wide range of temperature between 250 and 510°C.

Figure 4 presents differences between thermal decay dynamics of mixtures (60 t ha^{-1} of straw and charcoal, 180 t ha^{-1} of farmyard manure and sheep faeces) and non-fertilized soils calculated for every soil type (LTAEs, sites) separately. It reveals similar changes in all soil types under the influence of organic amendments, which causes individual changes in temperature ranges between 200 and 550°C. In turn, TG-fingerprinting could be possible for detection of organic amendments. However, in temperature ranges from 30 to 200°C, peak shifts appear to be dependent on soil type.

The temperature area used for organic carbon determination ($TML_{320–330}$) was influenced by thermal decay dynamics of organic amendments in a different way. For example, addition of straw with a peak temperature around 300°C (*Blanco* and *Almendros*, 1994; *Lopez-Capel* et al., 2006) had higher peak intensity. This leads to an overestimation of the carbon content. In contrast, charcoal mainly caused additional mass losses around 500°C (*Leifeld* et al., 2007; *Plante* et al., 2009; *Cimò* et al., 2014). These changes were not captured by $TML_{320–330}$ and resulted in an underestimation of organic carbon content of the mixtures of charcoal with soils using TG as

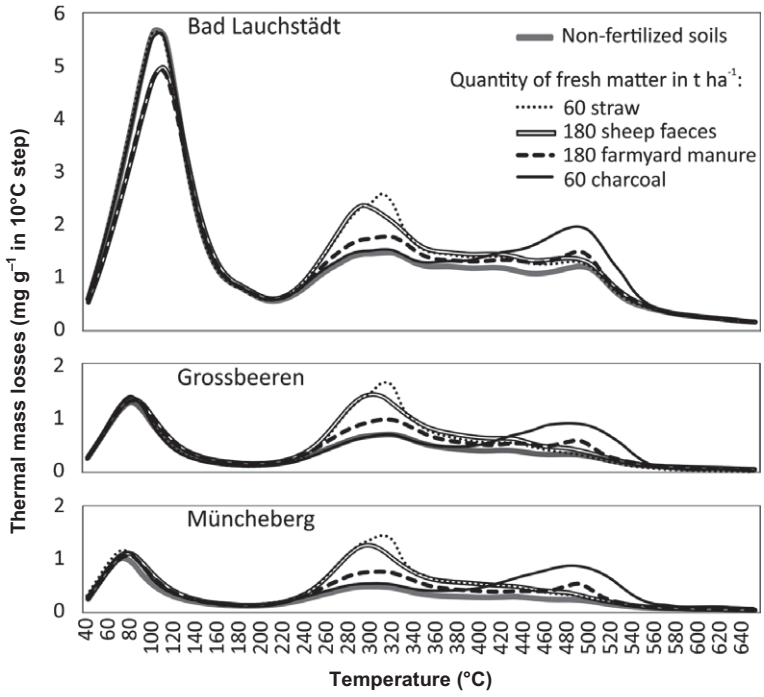

Figure 3: Means of thermal mass losses of soil from Bad Lauchstädt, Grossbeeren, and Müncheberg with added organic amendments in two quantities compared to non-fertilized soils (nothing added).

determination method. Following these considerations, a combined application of two or more of the amendments will increase uncertainties when using the TG method for detection of carbon in soils and of the quality of SOM. TML's ($TML_{120–130}$ and $TML_{520–530}$) were found to correlate with each other. Both of these temperature ranges can be used to predict soil clay content (*Siewert*, 2004). Our current study confirmed deviations of $TML_{520–530}$, because thermal stabile organic amendments produce mass losses above the level caused by clay content. This finding was suggested for indirect detection of black carbon in soils (*Leifeld* et al., 2007; *Siewert* and *Kučerík*, 2015).

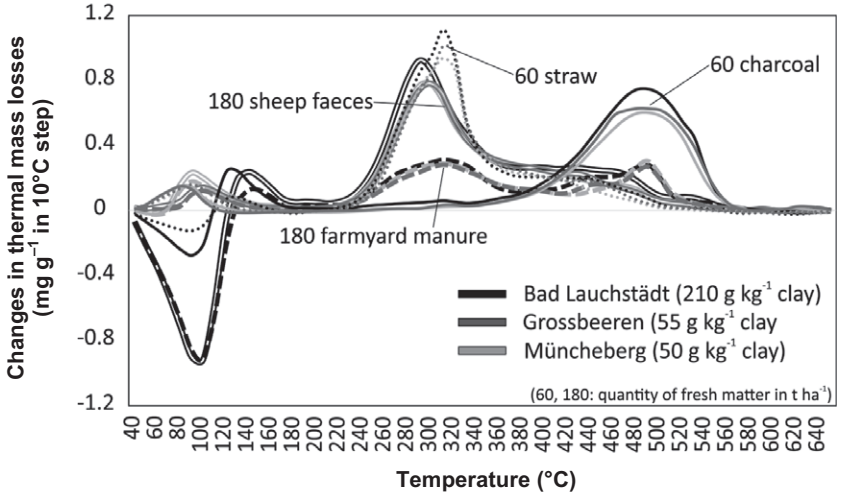

Figure 4: Changes in dynamics of thermal mass losses caused by highest quantities of added organic amendments at every site presented as differences between mixtures and of non-fertilized soils.

Figure 5 shows these data for investigated model experiments. The largest deviations from correlation between TML for clay content determination can be observed for the highest quantities of added charcoal because of the increased thermal mass losses at $TML_{520–530}$. In contrast, larger quantities of straw, farmyard manure, and sheep faeces produced a shift of results in direction of higher $TML_{120–130}$, which may be explained by additional water binding of organic amendments.

The higher thermal stability of charcoal (*Leifeld* et al., 2007; *Plante* et al., 2009; *Cimò* et al., 2014) caused shifts to higher TML 520–530°C values (y-axis). In case of fresh organic residues we found a trend of increased TML 120–130°C values (x-axis). However, this effect is difficult to quantify, because of the unknown impact of water-binding on thermal decay dynamics.

Another approach to detect changes in SOM is based on comparing measured mass loss on ignition (MLI) by estimation using both organic carbon and clay contents (*Kučerík* et al., 2016). Once the organic carbon and clay content can be calculated such as from TML_{330} and TML_{140} (*Siewert*, 2004), both measured and calculated MLI can be extracted from TG records (see Fig. 6a; with $MLI_{calculated} = 10 \times TML_{140} + 25 \times TML_{330}–2$ and $MLI_{measured} = TML_{110–550}$).

The MLI values vary as expected with soil types (LTAEs, sites), and with type and quantity of organic amendments. Within every LTAE, non-fertilized plots had the lowest values. Adding higher quantities of organic amendments resulted in increased MLI. The different levels of values between soil types hamper comparing of fertilization effects.

Figure 6b presents the differences between calculated and measured MLI. A site specific initial value could be detected for every type of soil (LTAE, sites) without any organic amendment fertilization over decades (small grey columns in Fig. 6b). In case of Müncheberg the non-fertilized soil had negative values. This may indicate a poorer supply with fresh organic matter in comparison to other sites. With increasing quantities of added straw, farmyard manure, and sheep faeces, the values increased in all soil types. Charcoal had contrasting effect. These results support suggestions about differences in MLI that could indicate changes in SOM supply of soils with higher content of biological degradable organic amendments (*Kučerík* et al., 2016).

Comparing different organic amendments, straw had the highest impact on predicted and measured MLI and is known for high biodegradability (*Hansen* et al., 2016).

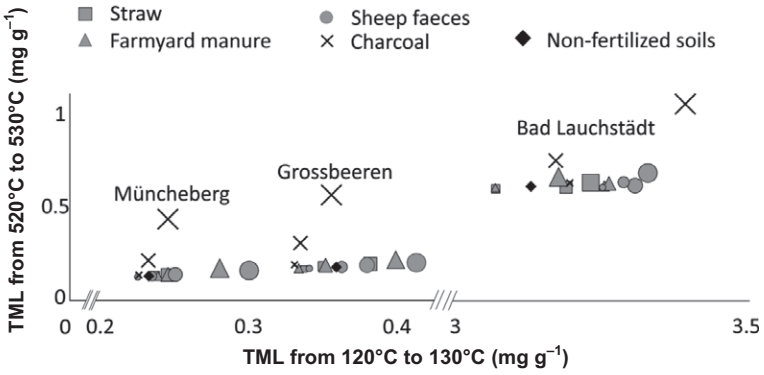

Figure 5: Interrelations between thermal mass losses at two temperature areas: $TML_{120–130}$ (linked to bound water and clay content) and $TML_{520–530}$ (linked to thermal stability and clay content) of soils (Bad Lauchstädt, Müncheberg, Grossbeeren) with organic amendments in different added quantities (presented in ascending order of different-sized icon, *e.g.*, 3 t ha^{-1}- smallest and 180 t ha^{-1}largest symbol only for farmyard manure and sheep faeces).

Farmyard manure and sheep faeces showed lower impact, because they already underwent transformation processes during digestion and composting. Charcoal as an example of a stable organic amendment (*Glaser* et al., 2002; *Kuzyakov* et al., 2009; *Lehmann* et al., 2009; *Li* et al., 2018) for soil property improvement showed contrasting changes in the relative supply of degradable organic carbon. It confirms the effect of the degree of biological degradation of the organic amendments on its detectability *via* thermal decay dynamics. This is a topic in a further study, which focusses on detectability of changes in thermal decay dynamics caused by biological degradation during incubation.

Furthermore, possible interactions with soil–clay minerals should be considered (*Pronk* et al., 2012; 2013) as a factor forming thermally more stable compounds. These results and the dynamics of thermal decay offer new approaches for the detection of qualitative changes in the SOM composition for practical issues.

4 Conclusion

Elemental analysis (EA) better captured changes in organic carbon content under the influence of different organic

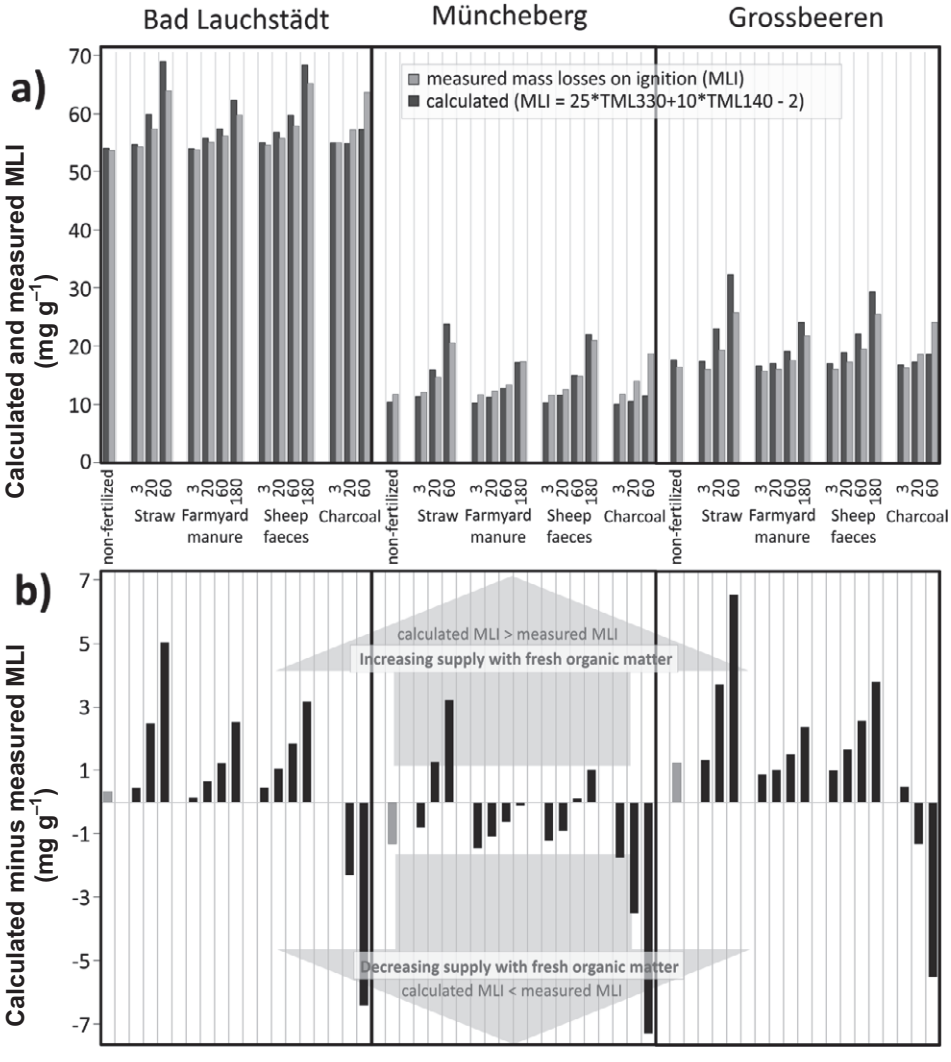

Figure 6: (a) Measured and calculated MLI (interrelation between MLI to TML_{140} and TML_{330}) for soils from LTAEs with added OA in different added quantities (t ha^{-1} fresh organic amendment); (b) differences of calculated by equation (MLI = 10 × TML_{140} + 25 × TML_{330}–2) minus measured MLI in order to assess the supply with fresh organic matter.

amendments and soil types with higher reliability and accuracy as compared to thermogravimetry (TG). However, both EA and TG methods do not allow the detection of very low quantities of added organic carbon due to limits of detection. Different peak temperatures in thermal decay dynamics of investigated types of organic amendments can cause both over- and underestimation of organic carbon content by using TG method. Due to these features, the peak heights and positions can be used as a fingerprinting tool which provides characteristics of the quality of added organic amendments independently of soil type. The tested method offer detection abilities for different types and quantities of added organic amendments. They could enable high sensitive detection of changes in soil organic matter composition by adding different organic fertilizers.

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