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Declaration of conformity

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List of Abbreviations

BeVOS	Bewertung der Versorgung von Böden mit Organischer Substanz
bf	Bare fallow
BL	Bad Lauchstädt
EA	Elemental analysis
eq	Equation
C	Carbon
CC	Charcoal
°C	Degree Celcius
°C min^{-1}	Degree Celcius per minute
CO_2	Carbon dioxide
D.F.	Degree of freedom
DTG	Differential thermogravimetric analysis
F	The variance ratio
FYM	Farm yard manure
Gb	Großbeeren
GV	Glühverlust
g-kg^{-1}	Gramms per Kilogramm
ha	Hectare
LTAEs	Long-term agricultural field experiments
LTML	Large thermal mass losses
mbf	Mechanical bare fallow
MLI	Mass loss on ignition
mL min^{-1}	Millilitres per minute
mg-g^{-1}	Milligramms per gramm
Mg-ha^{-1}	Megagramms per hectare
Mü	Müncheberg
N	Nitrogen
NaCL	Natriumchlorid
nf	Non-fertilization
N/A	Not analyzed

DOC	Dissolved organic carbon
OA	Organic amendments
OBS	Organische Bodensubstanz
p	the probability level
pF	Potenz von freier Energie des Wassers im Boden
POC	Particulate organic carbon
rSOC	Chemically resistant organic carbon
S+A-SOC	Organic carbon in the sand fraction and in stable aggregates
s+c-SOC	Organic carbon attached to silt and clay particles
SF	Sheep faeces
SOM	Soil organic matter
SOC	Soil organic carbon
ST	Straw
TG	Thermogravimetry
TML	Thermal mass losses
TMV	Thermische Masseverluste
TN	Total nitrogen content
t-ha^{-1}	Tons per hectare
WRB	World Reference Base

Summary

Suistainable land use today is challenged by increasing competition for plant production for food, feed and fuels and is accompanied by undesirable side effects such as enhanced soil degradation, eutrophication of aquatic ecosystems and emission of greenhouse gases. The development of sustainable land management systems requires a practical assessment of soil organic matter (SOM) as a driver of regulation processes for nutrient and water supply in soils and their fertility. Knowledge about the status of organic matter supply in agricultural soils can help to determine the behaviour of plant-available nutrient stocks and their cycles and is essential to mitigate side-effects of current land use.

The aim of this thesis was the experimental evaluation of thermogravimetry (TG) to assess the status of organic matter supply in agricultural soils. TG is an innovative analytical method for recording thermal mass losses (TML) during heating of soil samples from room temperature to 950 °C. The determination of TML in 10 °C temperature increments (TG indicators) is a central method of TG data evaluation. There is a very close correlation between selected temperature ranges and classically determined soil properties (organic carbon, total nitrogen and clay content). The regression parameters of these relationships can be used to estimate soil properties and to assess the quality of SOM.

Soil samples from different fertilization strategies of various long-term agricultural field experiments (LTAEs), artificial soil mixtures with added organic amendments (model experiments) as well as archived samples from research projects of cooperation partners were used. Investigations focused on the determination of soil properties using standard methods, the measurement of soil respiration, the analysis of dynamics of TML, and their comparison with a combined chemical and physical fractionation method. The latter is based on the determination of functional soil organic carbon (SOC) fractions differing in turnover times such as particulate organic carbon (POC), dissolved organic carbon (DOC), SOC in sand and stable aggregates (S+A-SOC), SOC attached to silt and clay particles (s+c-SOC) and a chemically resistant SOC fraction (rSOC).

The following aspects were considered to evaluate the suitability of TG to detect changes in soil organic matter quality: a) the thermogravimetric determination of soil properties, b) the detectability of changes in organic matter quality during the artificial mixing of different organic amendments with soil, c) the quantification of changes in SOM during biodegradation under controlled laboratory conditions, d) correlation of TG with results from the chemical-physical SOC fractionation.

Results confirmed the determinability of the carbon (C) content in soil samples via TML in small and large temperature ranges. Admixtures of organic amendments (e.g. plant residues, straw, sheep faeces) or thermally stable C - compounds (e.g. charcoal) falsified the C content determination depending on the amount and quality added and thus refer to limitations of the TG. Based on these deviations, in

combination with standard methods for C - analysis (elemental analysis - EA), new opportunities arise for distinguishing between C enriched during soil genesis and C from other sources (e.g. organic fertilizers and charcoal) independent on soil properties. The difference between the C content measured by EA and by TG would document the amount of carbon not derived from the soil, while the direction of the deviation would provide information on the origin of the carbon.

Similar results were obtained regarding the determination of clay content by TML between 120 °C and 130 °C (TML_{130}) and between 520 °C and 530 °C (TML_{530}). In this case, admixtures of plant residues, organic fertilizers and charcoal likewise had an effect on the dynamics of thermal mass losses. Plant residues induced higher mass losses at TML_{130}, whereas charcoal induced higher mass losses at TML_{530}. Additions of organic amendments thus simulate a higher clay content in soils. A comparison with the clay content from the reference analysis (pipette method) provided indications of differences in the SOM quality.

In laboratory experiments, the comparison of TML with soil respiration (120-day incubation experiment) revealed significant correlations regarding the biodegradability of organic amendments and fertilizers in soils. Incubation-induced changes in TMLs between 200 °C and 300 °C occur, for example, due to the degradation of straw and sheep faeces. At the same time, these mass losses showed close correlations to the CO_2-C evolution (R^2 = 0.96). In the case of incubation of samples with e.g. added farmyard manure, TMLs between 300 °C and 450 °C were changed, whereby close correlations to CO_2 -C evolution were also observed (R^2 = 0.95).

The development of TG indicators to assess SOM quality has not been completed yet due to the large number of new findings. For example, the differences between the measured loss on ignition (MLI = TML between 110 °C and 550 °C) and the predicted MLI by organic carbon (TML_{330}) and clay content (TML_{140}) reflect the short-term supply of SOM in artificial soil mixtures and in LTAEs with added organic amendments (e.g. straw, sheep faeces, farmyard manure and fresh plant residues). For example, organic amendments could be detected using the predicted MLI depending on the amount added to the soil. Also, the effects of organic fertilization across different sites (soil type) were similar. Modified evaluation algorithms resulted in better predictions about the supply of organic matter in soils. However, further experimental evidence is necessary.

Linking TG with a combined chemical and physical fractionation method revealed significant relationships between TML in large temperature ranges ($TML_{200-300}$, $TML_{200-450}$, $TML_{300-450}$ and $TML_{450-550}$) and SOC fractions in arable and grassland soils. Thus, in contrast to the determination of soil properties, new possibilities for fractionation of the SOM based on dynamics of TML could be provided. High coefficients of determination when comparing TML and POC (R^2 = 0.91) and DOC (R^2 = 0.76) as well as the "Active SOM Pool" (R^2 = 0.92) referred e.g. to similar statements of both methods about the availability of easily degradable SOM components. The coefficients of determination for the "Intermediate SOM pool" ($R^2 = 0.88$) consisting of S+A-SOC ($R^2 = 0.89$) and s+c-SOC ($R^2 = 0.70$), were significantly smaller. Probably, the thermal stability of SOM has no clear boundary for thermal decay in predefined large temperature ranges. No significant relationships between TMLs and the resistant carbon fraction (rSOC) could be found. As a result, the presumed relationships between TMLs (e. g. TML_{530}) and clay content as important factors influencing the stabilization of SOM were not detectable when compared to rSOC.

In summary, the results confirmed the applicability of TML as TG indicators for soil properties, biological degradability, and thermal stability of SOM for the assessment of organic matter supply in agricultural soils. This conclusion is based on model experiments under laboratory conditions and in long-term agricultural field experiments with different soil management strategies. However, TG has some limitations concerning the determination of soil properties in samples with added organic amendments and fertilizers. A combination of TG with standard methods offers advanced information regarding the contribution of organic amendments to SOM quality. Still, this study's findings indicate that the application potential of TG has not yet been fully exploited. For the development of new evaluation algorithms, special challenges are posed by the overlapping of unknown decay processes in thermal analysis.

Fast, simple, economical - with the application of thermogravimetry there is a high potential to solve an important problem of sustainable soil management - the assessment of the status of organic matter supply in agricultural soils.

Zusammenfassung

Die heutige Landwirtschaft wird durch den zunehmenden Wettbewerb um die Produktion von Pflanzen für Lebensmittel, Futtermittel und Kraftstoffe herausgefordert und ist von unerwünschten Nebenwirkungen wie Bodendegradation, Eutrophierung der aquatischen Ökosysteme und Emission von Treibhausgasen begleitet. Die Entwicklung nachhaltiger Nutzungssysteme erfordert eine praxisnahe Bewertung der organischen Bodensubstanz (OBS) als Spiegelbild der Regulationsprozesse für die Nährstoff- und Wasserversorgung in Böden und deren Fruchtbarkeit. Kenntnisse über die Versorgung von landwirtschaftlichen Böden mit organischer Substanz können dabei helfen, das Verhalten von pflanzenverfügbaren Nährstoffvorräten- und Kreisläufen zu bestimmen und somit zur Eindämmung von Nebenwirkungen (Eutrophierung) der aktuellen Landnutzung beitragen.

Ziel dieser Arbeit war die experimentelle Evaluierung der Thermogravimetrie (TG) zur Bewertung des Versorgungsgrades landwirtschaftlicher Böden mit organischer Substanz. TG ist eine innovative Labormethode zur Erfassung von thermischen Masseverlusten (TMV) bei der Erwärmung von Bodenproben von 25 auf 950 °C. Die Bestimmung von TMV in 10 °C Temperaturstufen (TG-Indikatoren) ist eine zentrale Methode der thermogravimetrischen Datenauswertung. Zwischen ausgewählten Temperaturbereichen und klassisch bestimmten Bodeneigenschaften (organischer Kohlenstoff, Gesamtstickstoff und Tongehalt) besteht eine sehr enge Korrelation. Die Regressionsparameter dieser Beziehungen können zur Abschätzung der Bodeneigenschaften und zur Beurteilung der Qualität der OBS verwendet werden.

Für die Evaluierung wurden Bodenproben aus unterschiedlichen Düngungsvarianten von mehreren landwirtschaftlichen Dauerfeldversuchen, künstliche Bodengemische mit organischen Rückständen (Modellexperimente) sowie Archivproben aus Forschungsvorhaben von Kooperationspartnern untersucht. Die Untersuchungen umfassten die Bestimmung der Bodeneigenschaften mit Standardmethoden, die Messung der Bodenatmung, die Analyse der Dynamik der TMV und deren Vergleich mit einer kombinierten chemisch-physikalischen Fraktionierungsmethode. Letztere basiert auf der Bestimmung von organischen Kohlenstofffraktionen wie z. B. partikulärer organischer Kohlenstoff (POC), gelöster organischer Kohlenstoff (DOC), organischer Kohlenstoff in der Sandfraktion und in stabilen Aggregaten (S+A-SOC), organischer Kohlenstoff gebunden in Schluff- und Tonpartikeln (s+c-SOC) sowie chemisch resistenter Kohlenstoff (rSOC).

Hauptbestandteile der Evaluierung waren a) die thermogravimetrische Bestimmung von Bodeneigenschaften, b) die Nachweisbarkeit von Veränderungen in der OBS beim Einmischen von organischen Rückständen in Böden, c) die Quantifizierung von Veränderungen in der OBS bei biologischen Abbau unter kontrollierten Laborbedingungen, d) der Vergleich von TG mit Ergebnissen aus der chemisch-physikalischen Kohlenstofffraktionierung.

Die Ergebnisse bestätigten die Bestimmbarkeit des Kohlenstoffgehaltes (C) in Bodenproben über TMV in kleinen und großen Temperaturbereichen. Beimengungen an frischen organischen Rückständen (z.B. Pflanzenrückstände, Stroh und Schafskot) oder thermisch stabilen C-Verbindungen (z.B. Holzkohle) verfälschen die Ergebnisse in Abhängigkeit von der zugegebenen Menge und verweisen damit auf Anwendungsgrenzen. Auf diesen Abweichungen aufbauend, bieten sich in Kombination mit Standardverfahren zur C - Analytik (Elementaranalytik - EA) neue Möglichkeiten zur Unterscheidung zwischen während der Bodengenese angereichertem C und C - Beimengungen aus anderen Quellen (z. B. organische Düngestoffe und Pflanzenkohle) in Abhängigkeit von den Bodeneigenschaften.

Ähnliche Aussagen wurden hinsichtlich der Bestimmung der Tongehalte über die TMV zwischen 120 °C und 130 °C (TMV_{130}) sowie zwischen 520 °C und 530 °C (TMV_{530}) bestätigt. Auch hier wirken sich Beimengungen an frischen Pflanzenrückständen, organischen Düngestoffen und Pflanzenkohle aus. Frische Pflanzenrückstände induzieren höhere Masseverluste bei TMV_{130}, Pflanzenkohle hingegen bei TMV_{530}. Beimengungen von organischen Rückständen täuschen so einen höheren Tongehalt vor. Ein Vergleich mit dem klassisch bestimmten Tongehalt (Pipette Methode) liefert Hinweise auf Unterschiede in der OBS-Qualität.

Wichtige Erkenntnisse zur biologischen Abbaubarkeit von organischen Rückständen und Düngern in Böden ergaben sich bei der Gegenüberstellung von TMV mit der Bodenatmung in Laborexperimenten (120-Tage-Inkubationsexperiment). Inkubationsbedingte Veränderungen in den TMV zwischen 200 °C und 300 °C treten z.B. durch die Umsetzung von Stroh und Schafskot auf. Diese Masseverluste zeigten zugleich enge Korrelationen zur CO_2–C- Freisetzung ($R^2 = 0{,}96$). Bei der Inkubation von Proben mit z. B. Stallmist werden auch TMV zwischen 300 °C und 450 °C beeinflusst, wobei ebenfalls enge Korrelationen zur CO_2 –C- Freisetzung nachgewiesen wurden ($R^2 = 0{,}95$).

Noch nicht abgeschlossen ist die Validierung komplexer TG-Indikatoren der OBS-Qualität auf Grund der Vielzahl neuer Erkenntnisse. So spiegeln beispielsweise die Unterschiede zwischen gemessenem Glühverlust (GV = TMV zwischen 110 °C und 550 °C) und vorhergesagtem GV mittels organischen Kohlenstoff (TMV_{330}) und Tongehalt (TMV_{140}) die kurzfristige Versorgung mit OBS in künstlichen Bodengemischen und Dauerfeldversuchen mit zugesetzten organischen Rückständen (z.B. Stroh, Schafskot, Stallmist und Pflanzenreste) wider. So konnten bei Einmischung frischer organischer Rückstände unter Laborbedingungen eindeutig proportional zur Menge steigende Werte zwischen gemessenen und vorhergesagten GV nachgewiesen werden. Außerdem waren Wirkungen organischer Düngung über unterschiedliche Standorte und in Abhängigkeit der Bodenart vergleichbar. Modifizierte Auswertungsalgorithmen führten zu besseren Vorhersagen des Versorgungsgrades landwirtschaftlicher Böden mit organischer Substanz. Es sind jedoch weitere experimentelle Untersuchungen erforderlich.

Die Verlinkung von TG mit einer chemisch-physikalischen Fraktionierungsmethode ergab signifikante

Zusammenhänge zwischen TMV in weiten Temperaturbereichen ($TMV_{200\text{-}300}$, $TML_{200\text{-}450}$, $TMV_{300\text{-}450}$ und $TMV_{450\text{-}550}$) und SOC-Fraktionen in Acker- und Grünlandböden. Damit ergeben sich - im Unterschied zur Bestimmung von Bodeneigenschaften – weitere Möglichkeiten zur Fraktionierung der OBS auf Grundlage der thermischen Zerfallsdynamik. Hohe Korrelationskoeffizienten bei dem Vergleich zwischen TMV zum POC ($R^2 = 0{,}91$) und DOC ($R^2 = 0{,}76$) sowie zum „Aktiven OBS Pool“ ($R^2 = 0{,}92$) verweisen z.B. auf vergleichbare Aussagen beider Methoden zu umsetzbaren OBS-Bestandteilen in Grünlandböden. Bei dem “Intermediären OBS-Pool”, bestehend aus S+A-SOC ($R^2 = 0.89$) und s+c-SOC ($R^2 = 0.70$), nimmt die über Korrelationskoeffizienten bewertete Vergleichbarkeit ab ($R^2 = 0.88$). Möglicherweise hat die thermische Stabilität der OBS keine eindeutige Zerfallsgrenze in vordefinierten Temperaturbereichen. Bei der resistenten Kohlenstofffraktion (rSOC) fanden sich keine signifikanten Beziehungen zu TMV. Die erwarteten Beziehungen zwischen TMV (z. B. TMV_{530}) zum Tongehalt - als wichtiger Einflussfaktor auf die Stabilisierung der OBS - waren im Vergleich zum rSOC nicht nachweisbar.

Die Ergebnisse dieser Doktorarbeit bestätigten die Anwendbarkeit von thermischen Masseverlusten als TG-Indikatoren für Bodeneigenschaften, biologische Abbaubarkeit und thermische Stabilität der OBS für eine Bewertung des Versorgungsgrades landwirtschaftlicher Böden mit organischer Substanz. Diese Schlussfolgerung basierte auf Modellversuchen unter Laborbedingungen und auf landwirtschaftlichen Dauerfeldversuchen mit verschiedenen Bodenbearbeitungsstrategien. TG zeigt jedoch Anwendungsgrenzen für die Bestimmung von Bodeneigenschaften in Proben mit frisch zugesetzten organischen Rückständen. Eine Kombination aus TG und Standardmethoden liefert aber detaillierte Informationen über den Beitrag von organischen Rückständen zur OBS - Qualität. Dennoch weisen die gewonnenen Erkenntnisse auf eine unvollständige Widerspiegelung des Anwendungspotentials der TG hin. Eine besondere Herausforderung für die Entwicklung neuer Auswertealgorithmen ergibt sich aus der Überlagerung unbekannter Zerfallsprozesse bei der thermischen Analyse.

Schnell, einfach, kostengünstig! Mit der Anwendung der Thermogravimetrie besteht ein hohes Potenzial zur Lösung eines wichtigen Problems der nachhaltigen Bodenbewirtschaftung: die Bewertung des Versorgungsgrades landwirtschaftlicher Böden mit organischer Substanz!

Chapter One – Synthesis: Thermogravimetry – a promising technique to assess the status of organic matter supply in agricultural soils

1 Introduction

1.1 Soils and agriculture

Soils are the key components in terrestrial ecosystems, which preserve and sustain life, and provide feedback to the other components i.e. water, atmosphere and vegetation (*Minasny* et al., 2015). Therefore, soil is the basis of natural plant growth and of agricultural communities (*Doran* and *Zeiss*, 2000).

The world's land (soil) surface amounts to 13.4 billion hectare (ha), of which 5 billion ha (38 % of land surface) are used for agriculture (*Johnson* et al., 2017). This agricultural area is the base for the annual production of maize, grain, rice and soya beans. From agricultural areas are produced approx. 1.1 Billion tonnes of maize (*Henrich*, 2019b), 2.7 Billion tonnes of grain (*Henrich*, 2019a), 497.9 Million tonnes of rice (*Henrich*, 2019c), and 347 Million tonnes of soya beans (*Henrich*, 2019d). This enormous agricultural production which has to be increased continuously requires high demands on the soil and an appropriate land management including high-yielding varieties, organic and chemical fertilizers, mechanisation and irrigation.

Soils are not only suppliers for primary products such as food, fibbers, animal feed, and biomass for fuel production (*Weil* and *Brady*, 2016), but also the world's largest terrestrial carbon reservoir (*Jobbágy* and *Jackson*, 2000).

Agricultural soils are central to human welfare (*Kleber* and *Lehmann*, 2015). Thus, the thin layer of soil covering the earth's surface is an important interface between agriculture and the environment (*Doran* et al., 1996). Humanity needs agricultural soils to produce healthy and vigorous plant products. That only works if we pay attention to the quality of the soil. *Karlen* et al. (1997) defines soil quality as "the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation."

Soil quality can change massively over time due to human impact. It can improve through sustainable land management, considering different soil functions, but can also be adversely affected by wrong decisions that focus only on individual functions, such as monocultures and high crop productivity. Therefore, holistic thinking is required for a balance between soil function for agricultural productivity, environmental quality and plant and animal health for sustaining optimal soil quality (*Doran*, 2002).

Today's modern agricultural practice already has the knowledge needed to maintain healthy and fertile soils, because this is the only source of high and robust crop yields. Nonetheless, farmers generally manage their land to maximise its benefits in the short-term rather than with a longer-term perspective of optimising land use. This means that they jeopardize the longer-term functionality of soils being highly important for many ecosystem services (*Barrios* et al., 2006). Thus, a change of mind in agriculture is needed to bring together short-term benefits (over a growing season) with long-term soil health perspectives in a holistic way. Such a rethinking, however, requires a solid scientific base. Science must provide farmers with reliable indicators of the quality of their soils.

The question now arises, which indicator is the most suitable one? One of the main key indicators of soil quality in agriculture is soil organic matter (*Arshad* and *Martin*, 2002; *Andrews* et al., 2004).

1.2 The Importance of soil organic matter (SOM)

SOM is the most crucial part of the soil, consisting of plant, animal and microbial residues at various stages of decomposition, biomass of soil microorganisms and substances produced by plant roots and other soil organisms (*Trumbore*, 1997; *Weil* and *Brady*, 2016; *Amelung* et al., 2018). SOM can be fractionated into two main components: active or labile SOM and relatively stable SOM (*Lal*, 2016). It is associated with many soil chemical, physical and biological properties and a key factor of terrestrial ecosystem productivity (*Gregorich* et al., 2015). In soils, organic matter can be stabilized by three mechanisms: (i) its biochemical resistance, (ii) the formation of organo-mineral complexes by chemical interactions with minerals and (iii) the physical separation from decomposers by e.g. occlusion in soil aggregates (*Lefèvre* et al., 2014). One of the most important mechanism is the formation of organo-mineral complexes due to the chemical bonding of SOM to clay (*Singh* et al., 2018). The clay content and the type of clays in soils significantly influence carbon stabilization (*Hassink*, 1997a).

As a result, the dynamics of SOM plays a significant role in the global carbon cycle (*Field* et al., 2007; *Conant* et al., 2011; *Dignac* et al., 2017) and it is accepted as elementary parameter to the sustainability of land use (*Doran*, 2002; *Amelung* et al., 2018; *Kleber* and *Lehmann*, 2015). In the soil, under constant environmental and vegetation conditions, there is a balance between the supply and degradation of organic matter, which is characterised by a typical SOM content (*Amelung* et al., 2018). However, climate change is increasing the pressure on SOM in addition and in relation to ongoing changes in agricultural land management (*Franko* and *Merbach*, 2017).

Therefore, information on the multifunctional contribution of SOM to soil quality is required (*Carter*, 2002). *Weil* and *Brady* (2016) suggest that the quantity and composition of SOM are essential factors in determining soil quality.

In agricultural soils, fertilizers and organic amendments, such as straw, farmyard manure, green manure, liquid manure, and fermentation residues are frequently used to increase the SOM content (*Haynes* and *Naidu*, 1998; *Körschens*, et al. 2013). Black carbon-based fertilizers such as charcoal and biochar have been used in the last few years in long-term agricultural field experiments in order to transfer their advantages as soil improvers into practice. Studies by *Glaser* et al. (2002) showed that charcoal is responsible for maintaining high SOM values and available nutrients in soils.

All of these fertilizers consist of biodegradable and stabilized organic carbon in different proportions (*Sarma* et al., 2017). In order to understand the degradability of SOM in agricultural soils, a distinction must be made between degradable carbon pools (subject to rapid oxidation by soil organisms within months) and stable carbon pools (stabilized by various mechanisms for years). Only with this information, it is possible to give specific answers about the behaviour and transformation of SOM in agricultural soils and their sustainability.

For recent decades, a fundamental change has taken place in agriculture. Today, the nutrient supply of plants is mainly provided by mineral fertilisation (*Pacanoski*, 2009). In addition, however, organic fertilizers from plant and animal production (organic residues) are widespread used in agricultural practice in order to increase SOM supply, biological activity, nutrient availability (*Bending* and *Turner*, 1999; *Lugato* et al., 2014; *Schröder* et al. 2016), and improve crop yields (*Haynes* and *Naidu*, 1998; *Körschens* et al., 2013) In order to measure soil quality of agricultural land, it is necessary to analyse the quantity and composition of SOM (e.g. organic carbon, amendments, and fertilizers).

1.3 Current challenges in the assessment of SOM as an indicator of soil quality

Carbon plays a key role for all organic substances. Soil organic carbon (SOC) is used to quantify SOM as a base information of soil quality (*Lal*, 2016). This term is particularly important, since most methods for determining SOM actually measure the carbon in the material and then use a conversion factor (e.g. SOC x 1.724 = SOM) to estimate the SOM content (*Weil* and *Brady*, 2016).

In recent decades, a number of analytical methods (qualitative, semi-quantitative and quantitative) have been used to measure the SOC content under laboratory conditions (*Schumacher* et al., 2002; *Colombo* et al., 2014). Choosing the method for SOC content determination is often a difficult decision, both in science and in practice, as it can also be challenging to estimate the SOC content and accurately assess the rate of change over time (*Brye* and *Slaton*, 2003).The most important factors in the selection of a specific method are reliability, reproducibility, time efficiency, sample throughput, and costs (*Lettens* et al., 2007; *Pallasser* et al., 2013; *Jandl* et al., 2014). In agriculture practice, these factors are decisive for the implementation of the method.

Typical SOC measurements are based on titrations while other use gravimetric, volumetric, spectrophotometric, or chromatographic methods (*Schumacher* et al., 2002). Widely applied methods are the Walkley-Black method (wet oxidation of organic carbon) (*Walkley* and *Black*, 1934; *Gelman* et al., 2012), loss on ignition (determination of weight percent organic matter) and dry combustion by elemental analysis with CO_2 detection (*Ball*, 1964, *Dean*, 1974; *Nelson* and *Sommers*, 1982; *Wang* et al., 2013). Other approaches are based on infrared spectroscopy, e.g. Middle-Infrared Spectroscopy and Fourier Transform Infrared spectroscopy. These methods are powerful tools for the study of mineral and organic components of soils by identification of functional groups, e.g. carbohydrates, lignin, cellulose, fats and proteins and analysis of a large number of soil samples (*Tinti* et al., 2015).

As already explained in the previous section, the analysis of SOC is an important tool for assessing organic matter in agricultural soils (*Haynes*, 2005). Despite the well-known importance of SOM, limit and guiding or reference values for the content of SOC are still missing (*Wessolek*, 2008). Reasons are insufficient knowledge of the complexity of processes and the diversity of organisms and substances in the soil. *Kleber* and *Lehmann* (2015) revealed that SOM research is particularly difficult because organic compounds are thoroughly mixed with and often adhere to soil minerals.

The critical comparison of different methods is essential for the assessment of the quantity and composition of SOM if it should be used as a key parameter for soil quality. Nevertheless, monitoring changes in SOM is still a challenging task today (*Jandl* et al., 2014). Maybe, identification and explanation of temporal changes in SOC contents are not the most important scientific objectives we have to solve. The right questions might be: How is SOC linked to soil quality? What fraction of SOC is changing?

This requires methods that can do much more than just reflecting the SOC content. Analytical methods and parameters are required that can map soil quality, such as microbial respiration by SOM decomposition during incubation experiments (*Paul* et al., 2006). This is an effective method for characterizing biological processes and mineralization in soils (*Mohanty* et al., 2011; *Peltre* et al., 2013; *Nguyen* et al., 2016; *Schiedung* et al., 2016a; *Xu* et al., 2017). It provides information on the stabilized and degradable fraction of organic carbon in soil available to heterotrophic organisms (*Hopkins*, 2007).

Hassink et al. (1997b) used a new size and density fractionation to isolate SOM fractions that differ in stability and estimated the amount of SOM that can be preserved in different soils. The use of such physical fractionation in SOM turnover studies increased steadily in recent years. It allows the separation of sand-size organic matter (labile pools) and the observation of stabilized components of SOM which is associated with mineral particles of higher density (*Tiessen* and *Stewart*, 1983; *Barrios* et al., 1996; *Christensen*, 2001). *Zimmermann* et al. (2007) combined physical and chemical fractionation methods to obtain more information about functional SOC fractions with different turnover times in soils.

Thermal analysis methods (e.g. thermogravimetry, differential thermal analysis and differential scanning calorimetry) are widely used to search for relationships between the dynamics of thermal decay and the biological stability of SOM (*Siewert*, 2004; *Leifeld*, 2007; *Plante* et al., 2009; *Peltre* et al., 2013; *Kučerík* et al., 2013; *Barros* et al., 2016). Many authors found correlations between thermoanalytical data and the SOC content and stabilization mechanisms of SOM (*Kuzyakov* et al., 2009; *Wei* et al., 2014; *Schiedung* et al., 2016b). The simplicity of thermal analyses and the possible reflection of biological processes as an essential property of soil make them attractive and promising (*Siewert* et al., 2012).

In today's agricultural soils the SOM content is very often reduced and too small for a sufficient nutrient supply and sustainable agricultural production. There is a lack of methods for the practical evaluation of the status of SOM regarding its degradability and nutrient supply and procedures based on this for an economically viable control of the SOM content. Skilled farmers therefore tend to prefer the use of mineral fertilizers irrespective of environmental risks such as nitrate contamination of groundwater. Fertiliser regulations are intended to reduce the discrepancy between economic interests and the ecological consequences of the use of mineral fertilisers. On the other hand, a reliable assessment of the transformation of organic matter in soils would motivate farmers with economic arguments to reduce the ecological consequences, because using the nutrient release potential of the SOM allows higher yields with less environmental impact. An assessment of the soil status regarding SOM supply should indicate the level when fertilization (organic and mineral) can be reduced and which measures should be taken by arable and plant cultivation to improve the SOM level of the soil. The interest of farmers in agricultural systems with high yield stability, in an optimised nutrient supply of plants and in the need to reduce nutrient losses (e.g. nitrate contamination of waters) is growing steadily.

In this dissertation, the close link between science and practice will contribute to the public perception of productive land use and soil as the basis of life. It will help to initiate a key technology of the future that combines economic prosperity with quality of life through high-quality food and feed, sustainable production of raw materials for the bioeconomy and reducing environmental risks. An assessment of SOM in agricultural practice is therefore a starting point for technologies that can mitigate negative environmental impacts and combine this with economic benefits.

1.4 Main objectives

The aim of this work is the experimental evaluation of thermogravimetry to assess the status of organic matter supply in agricultural soils.

The focus of this work is to test previously known and new TG indicators, which show the relationships between thermal mass losses and soil properties (organic carbon, total nitrogen and clay), organic amendments and fertilizers, and their influence on functional SOC fractions with different turnover times in agricultural soils.

In particular, the work focuses on:

1. Analysis of SOC content using defined temperature ranges of thermal mass losses
2. Detectability of organic amendments with different thermal stabilities in soil samples using different ranges of thermal mass losses
3. Comparison between biological and thermal stability of SOM
4. Linking thermogravimetric data with soil properties and SOC fractions
5. Searching new TG indicators determining SOM composition and soil quality

The following hypotheses have been tested:

I. TG-fingerprinting is applicable for the detection of soil organic carbon and identification of different organic amendments in soils regardless of the soil type (chapter two)
II. The biological and thermal stability of organic fertilizers in agricultural soils can be determined using thermal mass losses (chapter three)
III. Linking thermal mass losses in selected temperature areas with soil properties could provide additional information about SOM stability (chapter four)
IV. Thermogravimetric indicators can be an additional tool to assess SOM stability besides traditional chemical-physical SOC fractionation (chapter five)

The topics of the following publications are intended to support the hypotheses as follows:

Chapter two: The main objective of the study is to investigate opportunities to detect 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 ranges of thermal mass losses.

Chapter three: This study focuses on the detectability of changes in thermal decay dynamics caused by the microbiological degradation of SOM in laboratory incubation experiments. The aim is to discover and validate temperature areas with the most informative values about the degradability of organic fertilizers and SOM in dependency on soil type.

Chapter four: The aim of this work is to answer the question about the meaning and potential functioning of thermogravimetric fractions (large thermal mass losses) and to validate the obtained relationships by predicting the temperature areas in an independent soil sample set.

Chapter five: The main focus of this work is the investigation of relationships between thermal mass losses and functional SOC fractions with different turnover obtained by the procedure of (*Zimmermann* et al. 2007) in top- and subsoils of temperate grassland and arable soils.

2 Methodological Approach

2.1 General approach

The Investigation is based on the combination of thermogravimetric data (ranges of thermal mass losses) with established reference methods to assess organic matter of soil samples from:

I. model experiments (artificial soil mixtures spiked with different organic amendments)
II. long-term agricultural field experiments and permanent agricultural soil monitoring areas with different fertilization, cultivation and soil management strategies
III. various geographical origin and land management

2.2 Experimental areas and soil description

The samples derived from four separate soil sample sets (compiled for the selected laboratory experiments).

For chapter two and chapter three, soils were used from three different long-term agricultural field experiments (LTAEs) in Germany (Table 1.1 and Table 1.2). The first site is located at the Helmholtz Centre for Environmental Research (UFZ) in Bad Lauchstädt (Saxony-Anhalt) with a mean annual precipitation of 481 mm and a mean temperature of 8.9 °C (*Körschens* and *Pfefferkorn*, 1998). The second site is situated at the Leibniz Institute of Vegetable and Ornamental Crops (IGZ) in Grossbeeren (Brandenburg) with a mean annual precipitation of 521 mm and a mean temperature of 8.4 °C (*Rühlmann*, 2009). The third site belongs to the Leibniz Centre for Agricultural Landscape Research (ZALF) in Müncheberg (Brandenburg) and had a mean annual precipitation of 525 mm and a mean temperature of 8.6 °C (*Barkusky*, 2009). Detailed information of the soil types and characteristics are provided in table 1 and table 2. In chapter four different natural soils not disturbed by humans and soils under different land management from various regions worldwide were used (Table 1.3). Chapter five dealt with the investigation of archived soil samples from permanent agricultural soil monitoring sites in Bavaria (southeast Germany) (*Schubert*, 2002; *Wiesmeier* et al., 2014,Table 1.4).

Table 1.1: 1st compilation (Chapter two): Soil material of non-fertilized treatments from three different German long-term agricultural field experiments.

Location / Experiment	Coordinates	Sampling date	Soil type	Soil depth [cm]	SOC [g kg^{-1}]	Clay* [g kg^{-1}]	Investigated test factor	Sample number	Reference
Bad Lauchstädt V120 (Germany), Established 1902	51°24’N, 11°53’E	12.10.2015	Haplic Chernozem	0 – 30	16.1	210	Non-fertilized control	1	(*Körschens* and *Pfefferkorn*, 1998)
Müncheberg V140 (Germany), Established 1963	52°30’N, 14°6’E	22.10.2015	Albic Luvisol	0 - 30	5.0	50	Non-fertilized control	1	(*Barkusky*, 2009)
Großbeeren DV Trasse 2c (Germany), Established 1989	52°21’N, 13°19’E	15.10.2015	Arenic Luvisol	0 - 30	8.0	55	Non-fertilized control	1	(*Rühlmann,* 2009)

*The clay content was determined by pipette method

Table 1.2: 2nd compilation (Chapter three): Soils from different German long-term agricultural field experiments with various fertilization treatments, types of crop and soil management techniques.

Location / Experiment	Coordinates	Sampling date	Soil type	Soil depth [cm]	SOC** [g kg^{-1}]	Clay* [g kg^{-1}]	Investigated test factor	Sample number	Reference
Bad Lauchstädt V494 (Germany), Established 1983	51°24’N, 11°53’E	12.10.2015	Haplic Chernozem	0 – 30	20 – 46	210	Crop rotation (corn, bare fallow); Non-fertilized control; application of FYM (200 Mg ha^{-1} yr^{-1})	8	(*Franko* and *Merbach*, 2017)
Bad Lauchstädt V505a (Germany), Established 1988	51°24’N, 11°53’E	12.10.2015	Haplic Chernozem	0 – 30	18 – 27	210	mechanical fallow, succession of weed flora (self-greening)	8	(*Franko* and *Merbach*, 2017)
Müncheberg V140 (Germany), Established 1963	52°30’N, 14°6’E	22.10.2015	Albic Luvisol	0 – 30	6 - 7	50	Non-fertilized control; application of N (160 kg ha^{-1} yr^{-1}); N + FYM (160 kg ha^{-1} yr^{-1} + 12.8 Mg ha^{-1} 3rd yr^{-1} FYM); N + straw (160 kg ha^{-1} yr^{-1} N + 4 Mg ha^{-1} 2nd yr^{-1} straw)	16	(*Barkusky*, 2009)

*The clay content was determined by pipette method, **soil organic carbon (SOC) was determined by elemental analysis

Table 1.3: 3rd compilation (Chapter four): Soil samples from regions with contrasting climate conditions, vegetation cover, and parent materials, including both natural, not disturbed by human activity sites and soils under different land management.

Location	Coordinates	Sampling date	Soil type	Soil depth [cm]	SOC** [g kg^{-1}]	Clay* [g kg^{-1}]	Sample number	Reference
Western Siberia	51°34’ N - 56°54’ N; 82°51’ E - 86°00’ E	2000	Luvisols, Alfisols, Mollisols and Phaeozems	0 - 30	2.0 - 120	20 - 530	83	(*Siewert*, 2004; *Kučerík* and *Siewert*, 2014)
Long-term agriculture experiments in Western Europe	No data available	2003	Luvisols	0 - 30	30.0 – 44.0	40 - 420	53	(*Siewert*, 2004)
National Parks in Germany	No data available	2008	Luvisols and Alfisols	0 - 30	80.0 – 270.0	20 - 430	33	(*Siewert*, 2004; *Siewert* et al., 2012)
National Parks and biosphere reserves in South America	2°26’ S-50°54’ S; 68°44’ W-83°15’ W	2007-2009	Alfisols. Aridisols, Andisols and Oxisols	0 - 30	0 – 250.3	6 - 50	28	(*Kučerík* et al., 2013)
Western Siberia	49°59’ N-56°24’N; 83°28’ E-88°56’ E	2010	Chernozems, Mollisols, Phaeozems and Luvisols	0 - 30	3.9 – 82.3	11 - 46	33	(*Kučerík* et al., 2013)
Pacific North West of USA	37°43’ N-48°9’ N; 119°35’ W-124°40’ W	2011	Inceptisols, Andisols, Alfisols and Mollisols	0 - 30	7.6 – 105.9	7 - 46	21	(*Kučerík* et al., 2013)

Antarctica	No data available	1999	Entisols	0 - 30	50.0 – 35.0	-	27	(*Bölter* et al., 2001)
Long-term agricultural experiments in Gezira region (Sudan)	No data available	2001	Vertisols	0 - 30	25.0 – 84.0	400 - 650	23	(*Elias* et al., 2002)

*clay content was determined by pipette method, **soil organic carbon (SOC) was determined by elemental analysis

Table 1.4: 4th compilation (Chapter five): Archived soil samples from agriculturally used sites (arable land and grassland) in Bavaria (Germany) were selected representing the major soil types in Bavaria (for details see (*Wiesmeier* et al., 2014).

Location	Land use	SOC** [g kg^{-1}]	Clay* [g kg^{-1}]	Soil depth [cm] / soil horizons	Sample number	Reference
Bavaria (southeast Germany)	Arable land	10 - 28	150 - 480	topsoils ~0-30	16	(*Wiesmeier* et al., 2014)
		1 - 19	10 - 660	subsoils ~30-110	39	
	Grassland	11 - 82	110 - 470	topsoils ~0-30	25	
		1 - 20	70 - 640	subsoils ~30-110	64	

*clay content was determined by pipette method, **soil organic carbon (SOC) was determined by elemental analysis

2.3 Application of thermogravimetric analysis (TG)

TG is "a technique whereby the weight of a substance, in an environment heated or cooled at a controlled rate, is recorded as a function of time or temperature" (*Mackenzie*, 1969).

The differential thermogravimetric analysis (DTG, Figure 1.1) of complex samples has led to very simple patterns in which the rates of thermal decomposition are interpreted as continuous destruction of plant biomass of varying stability. It was found that most chemical and biological maturity levels correspond to the area-related peak values in the DTG curves (*Blanco* and *Almendros*, 1994).

The characteristics of such DTG curves are of great interest for the evaluation of the biological and thermal stability of organic matter in soil.

Siewert (2004) has shown that estimating the content of organic carbon, total nitrogen, clay and carbonates in soils is an additional approach of the TG method compared to traditional analytical methods.TG has the advantage of combining several analyses in one method with a simplified procedure and sample preparation.

For the TG measurements of the soil samples a thermo scale (Mettler-Toledo TGA/SDTA 851e) at the University of Applied Sciences in Dresden (Saxony, Germany) was used. The air-dried and sieved (2 mm screen) soil sample were placed in a ceramic pan and heated with a rate of 5 °C min^{-1} from 25 °C to 950 °C. The sample mass was recorded every 4 seconds or one measurement for 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). Soil sample conditioning at 76 % relative humidity excludes biodegradation at soil water content as close as possible to dry soils under field conditions (*Siewert*, 2001).

The primary data evaluation started with recalculation of mass losses to 1 g of soil and with reduction of data density to one mean thermal mass loss (TML) per 10 °C temperature increase (Figure 1.1). TML is usually given with lower and upper temperature limit. For example, TML_{330} describes TML from 320 °C to 330 °C.

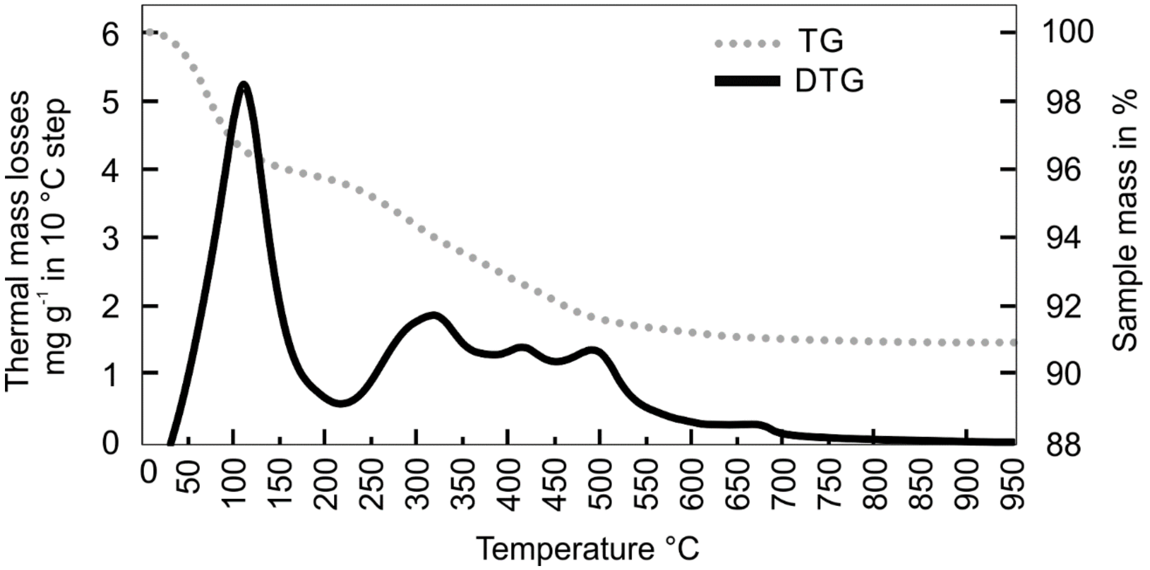


Figure 1.1: Thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG)

2.4 Experimental design

2.4.1 SOC content determination using TML (chapter two and chapter five)

Soil data from LTAEs (Table 1.1), artificial soil mixtures (Table 2.2) and archived soil samples from permanent agricultural soil monitoring sites (Table 1.4) were compared with thermogravimetric data (TML for SOC content determination). Therefore, two different approaches were used to study changes in SOC content. First the SOC contents artificially increased by organic amendments (straw, sheep faeces, farmyard manure, and charcoal) under laboratory conditions (artificial soil mixtures, N = 48) were determined with elemental analysis and compared with TML (*Tokarski* et al., 2018). Secondly, the SOC contents (determined by elemental analysis) of samples from permanent agricultural soil monitoring sites (arable and grassland soils, N = 144) were correlated with TML (*Tokarski* et al., 2019b). To compare these two methods with each other, the SOC contents were calculated from TML_{330} and TML_{350} (TG indicators) proposed by (*Siewert*, 2004) for SOC content determination because of the highest reliability and accuracy of this methods. Following equations were used:

$$\text{SOC content} = 1.18 \cdot \mathrm{TML}_{330} - 0.05 \qquad \text{(eq. a)}$$

and

$$\text{SOC content} = 1.48 \cdot \mathrm{TML}_{350} - 0.08 \qquad \text{(eq. b)}$$

2.4.2 Detectability of thermal stabilities of organic amendments in soil samples using TML (chapter two)

Soil data of selected artificial soil mixtures were compared with thermogravimetric data (TML for soil property determination). For this purpose, artificial soil mixtures spiked with organic amendments (N = 48) were carried out to determine SOM composition with both elemental analysis and TML (*Tokarski* et al., 2018). The following procedures for the detection of organic fertilizers was applied.

I. Comparison of SOC contents determined by both elemental analysis and TML for SOC content determination (TG indicator TML_{330})
II. Comparing dynamics of TML between 200 and 550 °C with individual peak analysis in distinct temperature ranges of soils spiked with different organic amendments.
III. Correlation analysis between TML_{130} and TML_{530} as TG indicators for the admixture of fresh plant residues and thermally stable carbon in soils as a function of soil clay content (*Siewert* and *Kučerík*, 2015) with selected equations:

$$\text{Soil clay content} = 4 \cdot TML_{130} + 10 \qquad \text{(eq. c)}$$

and

$$\text{Soil clay content} = 27 \cdot TML_{530} + 1 \qquad \text{(eq. d)}$$

2.4.3 Comparison between biological and thermal stability of SOM (chapter two and chapter three)

Soil data of LTAE`s with different fertilization treatments (N = 35, Table 1.2) and of selected artificial soil mixtures (N = 12, Table 2.2) were compared with thermogravimetric data (ranges of TML) (*Tokarski* et al., 2018; *Tokarski* et al., 2019a). Following approaches were used to investigate the biological and thermal stability of SOM.

I. Comparing measured mass loss on ignition (MLI) between 110-550 °C ($TML_{110\text{-}550}$) by estimation using TG indicators for SOC content (TML_{330}) and soil clay content (TML_{140}) (*Siewert*, 2004; *Kučerík* et al., 2016) for determining changes in SOM using the linear equation:

$$MLI_{calculated} = 10 \cdot TML_{140} + 25 \cdot TML_{330} - 2 \text{ and } MLI_{measured} = TML_{110\text{-}550} \qquad \text{(eq. e)}$$

II. Difference between calculated (relationship between TML_{140} and TML_{330}) and measured MLI ($TML_{110\text{-}550}$) for the determination of biodegradable SOM (*Kučerík* et al., 2016).
III. Comparison of changes in TML before and after incubation (CO_2-C evolution) of samples to discover temperature ranges with most informative value about the degradability of organic fertilizers and SOM in dependency on soil type (*Tokarski* et al., 2019a).

2.4.4 Linking thermogravimetric data with soil properties, thermal stability of SOM and SOC fractions (chapter four and chapter five)

Soil data of samples from different geographical origin and land management (N = 301, Table 1.3) (*Kučerík* et al., 2018) and archived soil samples from permanent agricultural soil monitoring sites (arable and grassland soils, N = 144, Table 1.4) were linked with thermogravimetric data (TG indicators and TG fractions) (*Tokarski* et al., 2019b). In order to validate the linear correlation between soils and selected soil properties, TG indicators for fractionation of SOM were developed. Furthermore, TML were correlated with functional SOC fractions of expected different turnover times including POC, DOC, SOC-S+A, SOC-s+c and rSOC (*Zimmermann* et al., 2007). For the qualitative assessment of SOM pools in soils, selected SOC fractions were mathematically combined. For this purpose, an active SOM pool was calculated as a sum of the C contents (mg C per g soil) in the DOC and POC fractions and an intermediate SOM pool as a sum of the C contents in the S + A-SOC and s + c-SOC fractions. The following procedures was applied:

I. Calculation of TG fractions in temperature areas larger than 10 °C (LTML), e.g. $\mathrm{LTML}_{200\text{-}300}$ corresponds to temperature area between 200 °C and 300 °C (the suffix indicates the index of LTML refers to the lower and upper temperature limit) (*Kučerík* et al., 2018).

II. LINEST function (linear least square curve fitting routine in Microsoft Excel®) was used to calculate a dependency between TML and LTML using following equations (*Kučerík* et al., 2018):

- linear one parametric fitting, i.e. we correlated one TML with a LTML (large thermal mass loss)

$$\mathrm{LTML} = a \cdot \mathrm{TML1} + b \qquad \text{(eq. f)}$$

- linear fitting with two parameters according to the equation

$$\mathrm{LTML} = c \cdot \mathrm{TML1} + d \cdot \mathrm{TML2} + e \qquad \text{(eq. g)}$$

- linear combination of three parameters according to the equation

$$\mathrm{LTML} = f \cdot \mathrm{TML1} + g \cdot \mathrm{TML2} + h \cdot \mathrm{TML3} + i \qquad \text{(eq. h)}$$

The letters a, b, c, d, e, f, g, h, i are fitted parameters.

III. Calculation of functional SOC fractions by the TG indicators TML and LTML using linear equations (*Tokarski* et al., 2019b):

- linear fitting with one parameter was carried out according to the equation

$$\text{SOC fractions} = a \cdot \mathrm{(L)TML}_1 + b \qquad \text{(eq. i)}$$

- linear fitting with two parameters was carried out according to the equation

$$\text{SOC fractions} = c \cdot TML_1 + d \cdot (L)\, TML_2 + e \qquad \text{(eq. j)}$$

The letters a, b, c, d, e, are fitted parameters.

3 Results and Discussion

3.1 Thermogravimetric-based fingerprint predictions of soil properties and soil organic matter stability (chapter two and chapter three)

SOC as the most important component of SOM has a significant influence on soil quality and is known to be dependent on soil properties including clay content (*Weil* and *Brady*, 2016; *Amelung* et al., 2018). Nevertheless, after decades of intensive basic research, no guideline or limit values for the SOC content could yet be established (*Wessolek*, 2008). Even a valid method for defining SOM quality for applied purposes of agricultural land use has not been developed so far.

This study focuses on the experimental evaluation of thermogravimetry as a solution to the current challenges in the assessment of the status of SOM supply in agricultural soils. When considering literature about thermal analytical techniques (*Leifeld*, 2007; *Plante* et al., 2009; *Méndez* et al., 2013; *Pallasser* et al., 2013; *Ghabbour* et al., 2014; *Hoogsteen* et al., 2015) the temperature ranges from 105 °C to 550°C (MLI) is cited as the most relevant for the thermal degradation of SOM. This large temperature range can be subdivided into many individual temperature intervals which allow accurate quantification of SOC content.

Siewert (2004) found that TG indicators in 10 °C increments such as TML_{330} and TML_{350} were correlated with SOC content determined by elemental analysis. This relationship is much closer for mass losses in small temperature intervals than for TML in large temperature ranges such as the measured MLI (105 - 550°C). This special feature of TG can be explained by the recording of overlapping biological, clay-dependent regulation processes of organic carbon in soils. However, these TG indicators are not considered to be suitable for carbon content determination in soils containing undecomposed plant residues, organic amendments and carbon of anthropogenic or geological origin.

In order to confirm these conclusions, laboratory model experiments with artificial soil mixtures spiked with organic amendments such as straw, sheep faeces, farmyard manure, and charcoal were carried out (chapter two). The results confirmed deviations in thermogravimetric SOC determination depending on the quantity of added organic amendments. This allowed new opportunities for the assessment of SOM quality. The difference between carbon content determined by both EA and TG methods seems to reflect the contribution of organic amendments to SOM which are not yet influenced by soil specific regulation processes.

Similar discoveries have been confirmed regarding the determination of clay content by TG and the standard pipette method. TG determines the clay content via mass losses of bound water in soils using TML_{130} or via TML_{530} as an indicator of clay dependent mass losses of organic matter (*Siewert*, 2004). The addition of fresh organic amendments such as straw, sheep faeces, and farmyard manure or charcoal to soils influence these two TMLs and, therefore, causes deviations. In comparison to the standard pipette method, the determination of clay content using TG produces different results.

Interestingly, it seems that the differences between the predicted (TG method) and measured (standard pipette method) clay content can provide information about the thermal stability of organic carbon in soils.

The combination of organic carbon and clay content determination allows the prediction of the MLI in soils (MLI = f [SOC, clay]). Any artificial addition of organic amendments to soils caused deviations between measured and predicted MLI. It was found that these deviations increase depending on the quantity of organic amendments added. Consequently, the function MLI = f [SOC, clay] reflects the supply of soil with organic matter, which was already found in long-term agricultural field experiments (*Kučerík* et al., 2016). These results confirm that organic amendments act as a driving factor for the biological transformation of degradable SOM in the soil environment (*Hansen* et al., 2016; *Kučerík* et al., 2016; *Soong* et al., 2018).

Degradable SOM is known as an indicator for determining soil quality when alternative land use and management practices are implemented (*Sparks*, 2019). Thus, applicable relationships between soil respiration and thermal stability of SOM in laboratory model experiments and in long-term agricultural field experiments were investigated in chapter three. It should provide a better understanding of the biological transformation of degradable organic amendments in agricultural soils.

The expected sequence of increase in CO_2-C evolution after artificial mixing of organic amendments to soils (model experiments) resulted in source-specific degradability (charcoal < farmyard manure < sheep faeces < straw). The CO_2-C evolution showed different turnover rates of organic amendments depending on clay and SOC content (*Singh* et al., 2018). It is assumed that interdependencies between clay and SOC content can explain different respiration rates of SOM (*Hassink*, 1997a). In sum, the degradation of organic amendments could be masked by clay-dependent organic carbon accumulation in soils or by carbon protection mechanisms.

Nevertheless, the comparison of different respiration rates is very important for the detection of degradable and stable organic amendments in agricultural soils. Anyway, farmers know from proper agricultural practices, that annual crop rotations and adapted fertilization strategies brings different quantities and qualities of organic matter into the soil. It seems more important to have a fast and reliable method for predicting biological transformation depending on the composition and quantity of SOM. TG could be a starting point for this. Therefore, determination of TML before and after 120 days of incubation showed different thermal stabilities of organic amendments in soils. The results indicated significant changes in TML of artificial soil mixtures spiked with organic amendments mainly in temperature ranges between 200 °C and 300 °C (plant residues) and between 300 °C and 450 °C (farmyard manure) before and after incubation. Correlation analyses between individual respiration rates and TML confirmed these results that the degradability of organic amendments can be accurately predicted using individual TG indicators such as TML_{300} and TML_{410}. In addition, a combination of different TMLs can provide further information that allows the determination of different organic fertilizers after their application to soils - a task that is currently being implemented with cooperation partners.

However, it should be noted that the close relationship between TG and the standard method for determining soil respiration was more limited in soils with long-term fertilization of farmyard manure and plant residues (in LTAEs). Reasons for this may be the long-term accumulation of organic amendments in the soil and the associated faster biological transformation of the degradable organic matter under field conditions. It seems that an equilibrium between the accumulation and transformation of organic amendments in soils can be established over time. Again, the interdependence of clay and SOC content plays a key role in the biological transformation (*Colman* and *Schimel*, 2013) and the accumulation of organic amendments in soil environments.

Additionally, the different composition of organic amendments used in agricultural practice can have a significant impact on their degradability in soils. These characteristics are mainly based on the storage and processing (composting) of organic fertilizers. Farmyard manure, for example, is a fertilizer that consists mainly of stable organic fractions rather than biodegradable components and therefore differs markedly in composition (*Mohanty* et al., 2011). It corresponds to the typical thermal decay dynamic of SOM in the temperature range between 200 °C and 550 °C (*Plante* et al., 2009; *Méndez* et al., 2013; *Pallasser* et al., 2013). This hampers the detection of degradable organic matter in agricultural soils under long-term fertilization with e.g. farmyard manure, slurry and fermentation residues using mass losses in small temperature intervals. Alternative organic amendments frequently used in agricultural practice include fresh plant residues or green manure (e.g. from, rapeseed straw, cereal straw, legumes etc.) (*Powlson* et al., 2008; *Hansen* et al., 2016). Such fresh organic fertilizers are usually degradable within a short period of time and essential for supplying the soil with important nutrients. TG analyses before and after incubation showed that the small temperature range around TML_{300} reflects the degradation of plant residues. Thus, this TG indicator is a useful tool for detecting degradable organic components derived of fresh plant residues in agricultural soils. Black carbon-based organic amendments such as charcoal are also used today in agricultural practice (*Nasar* et al., 2019). For example, various composts mixed charcoal are in widespread use to fertilize arable land. As mentioned before, such amendments are very stable and relatively difficult for micro-organisms to degrade. This was also demonstrated in our incubation experiments. Consequently, we could not detect any significant degradation of charcoal in soils (artificial soil mixtures) by TG after incubation.

In summary, chapter two and three have shown that the simultaneous use of thermogravimetric data (TG indicators) and standard reference methods for determining soil properties seems to be a future-oriented fingerprint model for assessing SOM and soil quality in agricultural practice. Methodological challenges in the detection of biodegradable and stable organic matter in agricultural soils remains open and validation of SOM fractionation methods in further experiments (*Poeplau* et al., 2018).

3.2 Linking thermogravimetric indicators with functional SOC fractions to assess SOM quality (chapter four and chapter five)

In recent decades, the determination of SOM thermal stability and functional SOC fractions with different turnover times using thermal and chemical-physical fractionation techniques has been proposed to quantify the impact of land use on soil quality (*Trumbore*, 1997; *Siewert*, 2001; *Zimmermann* et al., 2007; *Schmidt* et al., 2011; *Peltre* et al., 2013; *Wiesmeier* et al., 2014; *Schiedung* et al., 2017; *Poeplau* et al., 2018; *Giannetta* et al., 2018; *Miller* et al., 2019). These approaches were combined with thermal mass losses (thermal decay of SOM) and with respiration rates during laboratory incubation experiments (biological degradation and transformation of SOM).

The experiments confirmed the reflection of changes in thermal mass losses during biological transformation of SOM. As a result, a mathematical fractionation of SOM into active and intermediate pools using thermal mass losses was obtained. However, this approach was limited by overlapping thermal decay processes, which led to an insufficient delimitation of the temperature boundaries. This led to the following predefined temperature ranges for SOM fractions (chapter four), which were initially derived from autocorrelation analyses (*Siewert* and *Kučerík*, 2015):

A 30 °C to 100 °C ($LTML_{30-200}$)

B 100 °C to 200 °C ($LTML_{100-200}$)

C 200 °C to 300 °C ($LTML_{200-300}$)

D 300 °C to 450 °C ($LTML_{300-450}$)

E 450 °C to 550 °C ($LTML_{450-550}$)

F 110 °C to 550 °C ($LTML_{110-550}$)

Considering the unknown influence of physically and chemically bound water, temperature ranges **A** and **B** show an overlapping influence of soil clay and organic residues (chapter two). Range **C** as part of the total SOM thermal decay included correlations to soil organic carbon and nitrogen content and changes due to biodegradation of SOM compounds (chapter three). Temperature range **D** mirrors more stable SOM fractions with no direct impact of clay. In contrast, correlation with clay proved to be a specific feature of range **E**, which was masked by the thermal decay of coal-based residues (e.g. charcoal). Temperature range **F** reflects a modified approach to defining the total SOM content via MLI, with valuable indications on the supply of soils with fresh organic matter (chapter two).

If these predefined temperature ranges are linked with chemical-physical SOC fractionation, reliable conclusions about the thermal stability of SOM can be made (chapter five). POC and DOC as the active SOM pool were reflected in temperature range **D** only and not as supposed in temperature range **C**. This coincides with conclusions of different authors about uncertain relationship between thermo-oxidative and biological stability (*Lopez-Capel* et al., 2005; *Helfrich* et al., 2010; *Schiedung* et al., 2016b; *Peltre* et al., 2013; *Barré* et al., 2016). S+A-SOC and s+c-SOC as the intermediate pool was correlated in the combined temperature range **C** and **D**. However, the overlapping of thermal decay processes could be compensated by using individual TML in 10 °C temperature increase steps for the determination of soil properties (chapter two). When applying this approach to the chemical-physical SOC fractionation, the correlations between the results of both methods were significantly higher and reached coefficients of determination above 0.9. An exception was found for the chemically resistant SOC fraction (rSOC) as an indicator for inert or passive SOM (*Wiesmeier* et al., 2014), which was not related to clay content and therefore does not influence the long-term accumulation of organic carbon in soil. In contrast, thermal mass losses in range **E** and especially in TML_{530} showed a correlation with clay content in samples without coal-based or thermally stable residues.

These results are highly relevant for assessing the status of soil organic matter supply in agricultural soils. SOM fractions provide indications on degradable and stable organic carbon with different turnover times.

This is an important step as the organic carbon fractions can provide additional information on the composition and duration of organic amendments and fertilizers in agricultural soils. The prediction of different carbon fractions with TG-indicators (temperature ranges A - E) thus allows an assessment of organic matter, which can support the farmer in planning soil and fertilizer management strategies.

In summary, combining thermogravimetry with chemical-physical fractionation resulted in a favourable prediction of functional SOC fractions with different turnover times via mathematical SOM fractionation. Nevertheless, an assessment of the status of organic matter supply in agricultural soils via predefined thermal mass losses is hampered by interacting decay processes and stabilization mechanisms. It appears that the thermal stability of SOM has no clear thermal decay boundary which clearly differentiates between degradable and stable organic matter.

4. Research needs and perspectives

The methodology and evaluation presented in this scientific study demonstrated a selection of the most important findings for assessing the status of organic matter supply in agricultural soils. Future investigation should consider the following challenges:

Improvement of the evaluation algorithms for the dynamics of thermal mass losses:

I. Distinction between short- and long-term effects of organic fertilization on SOM in agricultural field experiments
II. Investigation of buried paleo soils as reference objects without inputs of degradable organic matter over a long period of time
III. Specific quality characteristics of SOM under influence of different land use (evaluation of existing samples and data set of Institute of Soil Science, Leibniz Universität Hannover)

Applied research needs for practical land use:

I. Quantification of the relationships between SOM quality, nutrient availability, and nutrient release (to increase yield and reduce nitrate pollution of water bodies)
II. Quantification of soil water storage capacity as a function of SOM quality
III. Validation of the relationships between SOM quality indicators, soil management practices (e.g. tillage, weed and disease control, mineral fertilizer application), and environmental risks (e.g. nitrate leaching, drought sensitivity, biodiversity, climate change)
IV. Investigation of different organic fertilizers and plant residues on SOM quality (including soil depend transformation processes, nutrient release etc.)

V. Distinction between site-specific and regional characteristics of SOM quality
VI. Statistical data analysis and interpretation of thermogravimetric indicators for the determination of SOM quality

Fundamental research:

I. Causal analysis of the relationships between thermal mass losses and organic carbon and clay content
II. Comparison and combination of thermogravimetric analysis with other methods such as near- and mid-infrared spectroscopy.

A first proposal focuses on an indicator database system to assess SOM quality in agricultural soils (BeVOS – **Be**wertung der **V**ersorgung von Böden mit **O**rganischer **S**ubstanz). This includes the establishment of a database to successively identify and distinguish general and local characteristics of the SOM composition caused by natural processes and anthropogenic influences on agricultural soils. In addition, it will allow a better application of the assessment of the status of organic matter supply in horticultural, forestry and urban soils in order to find a generally applicable approach that reflects the value of soils as the basis for life on our planet.

The indicators under development should reflect the following specifications:

1. The amount of carbon generated independently of the succession of geological or anthropogenic ecosystems (brown coal, charcoal, soot, ash, slag, microplastics)
2. Long-term supply of SOM reflecting decades of land management practice
3. Short-term supply of SOM reflecting the fertilization, crop rotation and cultivation practices applied during the growing season
4. Stabilisation of the SOM as an indication of the state of soil regulation processes and related processes that influence nutrient release or changes in soil water holding capacity via interactions between short and long-term SOM supply.

In addition, new indicators will be integrated. First examples show hints on determining biodiversity, nitrate release, field water retention capacity and regulated degradation processes of organic litter in forest soils or organic residues in fruit tree orchards.

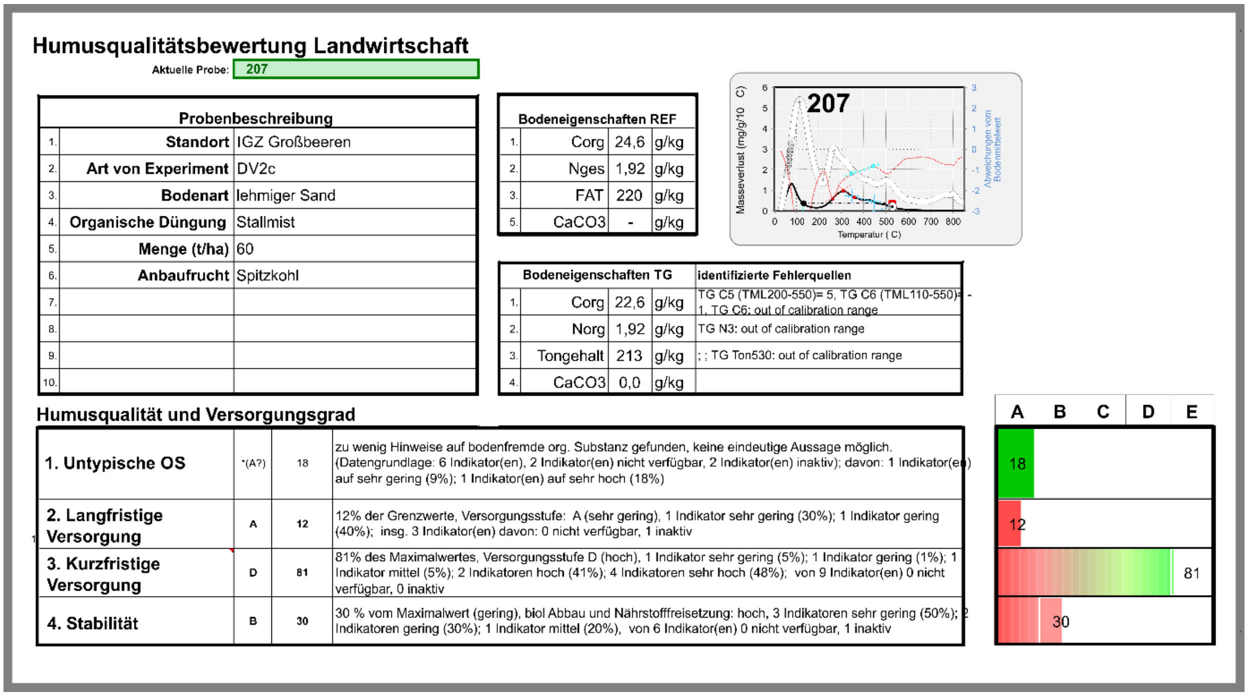
Figure 1.2 summarizes a first draft with already realized ideas for an automatic evaluation procedure using primary files from thermogravimetric analysis and linked database with Microsoft Excel®.

The application shows the following elements:

a) The required sample description (table Probenbeschreibung)
b) The soil properties determined by standard methods (table Bodeneigenschaften REF)
c) The soil properties determined by TG derived from the thermal mass losses, with information on possible sources of error in the thermogravimetric data (table Bodeneigenschaften TG)
d) An overview of the dynamics of thermal mass losses, including the main indicators, selected correlations between mass losses and other useful reference information
e) Summary information on the status of SOM supply according to the above-mentioned TG indicators, each calculated according to different algorithms (table Humusqualität und Versorgungsgrad, partially published, up to 12 indicators).

The table (Humusqualität und Versorgungsgrad) consists of a short description of the TG indicators (see above), a ranking list with the usual classification of fertilisation in German agricultural practice in 5 levels (from A: low supply or content to E: high supply or content), comments on the number of available, considered or inactive TG indicators used for the calculation, and a small graph with further visualised weighting information.

Further information is included in a research proposal for submission to a funding organisation.



Humusqualitätsbewertung Landwirtschaft

Aktuelle Probe: 207

	Probenbeschreibung	
1.	**Standort**	IGZ Großbeeren
2.	**Art von Experiment**	DV2c
3.	**Bodenart**	lehmiger Sand
4.	**Organische Düngung**	Stallmist
5.	**Menge (t/ha)**	60
6.	**Anbaufrucht**	Spitzkohl
7.		
8.		
9.		
10.		

	Bodeneigenschaften REF		
1.	Corg	24,6	g/kg
2.	Nges	1,92	g/kg
3.	FAT	220	g/kg
5.	CaCO3	-	g/kg

	Bodeneigenschaften TG			identifizierte Fehlerquellen
1.	Corg	22,6	g/kg	TG C5 (TML200-550)= 5, TG C6 (TML110-550)= -1, TG C6: out of calibration range
2.	Norg	1,92	g/kg	TG N3: out of calibration range
3.	Tongehalt	213	g/kg	; ; TG Ton530: out of calibration range
4.	CaCO3	0,0	g/kg	

Humusqualität und Versorgungsgrad

				A B C D E
1. Untypische OS	*(A?)	18	zu wenig Hinweise auf bodenfremde org. Substanz gefunden, keine eindeutige Aussage möglich. (Datengrundlage: 6 Indikator(en), 2 Indikator(en) nicht verfügbar, 2 Indikator(en) inaktiv); davon: 1 Indikator(en) auf sehr gering (9%); 1 Indikator(en) auf sehr hoch (18%)	18
2. Langfristige Versorgung	A	12	12% der Grenzwerte, Versorgungsstufe: A (sehr gering), 1 Indikator sehr gering (30%); 1 Indikator gering (40%); insg. 3 Indikator(en) davon: 0 nicht verfügbar, 1 inaktiv	12
3. Kurzfristige Versorgung	D	81	81% des Maximalwertes, Versorgungsstufe D (hoch), 1 Indikator sehr gering (5%); 1 Indikator gering (1%); 1 Indikator mittel (5%); 2 Indikatoren hoch (41%); 4 Indikatoren sehr hoch (48%); von 9 Indikator(en) 0 nicht verfügbar, 0 inaktiv	81
4. Stabilität	B	30	30 % vom Maximalwert (gering), biol Abbau und Nährstofffreisetzung: hoch, 3 Indikatoren sehr gering (50%); 2 Indikatoren gering (30%); 1 Indikator mittel (20%), von 6 Indikator(en) 0 nicht verfügbar, 1 inaktiv	30

Figure 1.2: Example database for the evaluation of short- and long-term supply of agricultural soils with organic matter.

5. Conclusion

The simple applicability, the high reliability and the reproducibility make thermogravimetric analysis in combination with other standard methods a promising tool for practical questions of SOM assessment in agricultural soils. However, the application is challenged by the overlapping of unknown thermal decay processes during heating of soil samples and by limited interactions with standard methods for the determination of soil properties, biodegradable and stable SOM and SOC fractions. These challenges can be seen as an advantage if the interrelations between different thermal mass losses in predefined temperature ranges are interpreted as indicators for soil-specific regulation processes.

Deviations from these relationships indicate the existence of organic amendments (plant residues, organic fertilizers) or carbon of anthropogenic (charcoal, soot, ash, slag, microplastics) and geological origin (brown coal) in soils. The degree of deviation provides information about the changing composition of the SOM as a semi-quantitative characteristic. In contrast to other methods for SOM quality determination, it was possible to evaluate this thermogravimetric approach via recovery rates in model experiments, during laboratory incubation and by correlating clay to SOC. This opens up new possibilities for the practical assessment of the soil status regarding the supply with SOM and its functional SOC fractions in the scope of soil regulation processes.

However, the use of thermogravimetry is challenged by the development of evaluation algorithms, the answering of questions of basic research, the discovery of correlations between SOM and nutrient release and water storage capacity depending on soil fertilization practice.

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Chapter Two: Contribution of organic amendments to soil organic matter detected by thermogravimetry

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Chapter Three: Detectability of degradable organic matter in agricultural soils by thermogravimetry

Tokarski, D., Šimečkova J., Kučerík, J., Kalbitz, K., Demyan, M. S., Merbach, I., Barkusky, D., Ruehlmann, J., Siewert, C.: Detectability of degradable organic matter in agricultural soils by thermogravimetry. – J. Plant Nutr. Soil Sci. 2019. 182, 729-740. DOI: 10.1002/jpln.201800516. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Chapter Four: Linking soil organic matter thermal stability with contents of clay, bound water, organic carbon and nitrogen

Kučerík, J., Tokarski, D., Demyan, M.S., Merbach, I. & Siewert, C. (2018): Linking soil organic matter thermal stability with contents of clay, bound water, organic carbon and nitrogen. – Geoderma 316, 38–46. © 2017 Elsevier B.V. All rights reserved. https://doi.org/10.1016/j.geoderma.2017.12.001. Reproduced with permission.

Chapter Five: Linking thermogravimetric data with soil organic carbon fractions

Tokarski, D., Wiesmeier, M., Doležalová Weissmannová, H., Kalbitz, K., Demyan, M. S., Kučerík, J., Siewert, C. (2019): Linking thermogravimetric data with soil organic carbon fractions. – Geoderma, 362. 15 March 2020, 114124. © 2019 Elsevier B.V. All rights reserved. https://doi.org/10.1016/j.geoderma.2019.114124. Reproduced with permission.

Appendix

List of publications

Tokarski, D., Kučerík, J., Kalbitz, K., Demyan, M. S., Merbach, I., Barkusky, D., Ruehlmann, J., Siewert, C. (2018): Contribution of organic amendments to soil organic matter detected by thermogravimetry. – *J. Plant Nutr. Soil Sci.* 181, 664–674.

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