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Combining a coupled FTIR-EGA system and in situ DRIFTS for studying soil organic matter in arable soils

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An optimized spectroscopic method combining quantitative evolved gas analysis via Fourier transform infrared spectroscopy (FTIR-EGA) and qualitative in situ thermal reaction monitoring via diffuse reflectance Fourier transform infrared spectroscopy (in situ DRIFTS) is being proposed to rapidly characterize soil organic matter (SOM) to study its dynamics and stability. A thermal reaction chamber coupled with an infrared gas cell was used to study the pattern of thermal evolution of carbon dioxide (CO₂) in order to relate evolved gas to different qualities of soil organic matter (SOM). Soil samples were from three different sites, i.e. (i) the Static Fertilization Experiment, Bad Lauchstädt (Chernozem) from treatments of farmyard manure (FYM), mineral fertilizer (NPK), combination (FYM + NPK) and control without fertilizer inputs, and cropped soils from the (ii) Kraichgau and (iii) Swabian Alb (Cambisols) areas, Southwest Germany. Soils from Kraichgau and Swabian Alb were further fractionated into particulate organic matter (POM), sand and stable aggregates (Sa + A), silt and clay (Si + C), and NaOCl oxidized Si + C (rSOC) to gain OM of different inferred stabilities. Fresh soil samples from the Kraichgau and Swabian Alb were incubated at 20 °C and 50 % water holding capacity for 490 days in order to measure soil respiration under controlled conditions. A variable long path length gas cell was used to record the mid-infrared absorbance intensity of carbon dioxide (2400 to 2200 cm⁻¹) being evolved during soil heating from 25 to 700 °C with a heating rate of 68 °C min⁻¹ during an initial ramping time of 10 min and holding time of 10 min. Separately the heating chamber was placed in a diffuse reflectance chamber (DRIFTS) for measuring the mid-infrared absorption of the soil sample during heating. Thermal stability of the bulk soils and fractions was measured via the temperature of maximum CO₂ (2400 to 2200 cm⁻¹) evolution (CO₂max). Results indicated that the FYM + NPK and FYM treatments of the Chernozem soils of Bad Lauchstädt had a lower CO₂max as compared to both NPK and CON treatments. On average CO₂max in Bad Lauchstädt was much higher (447 °C) as compared to the Kraichgau (392 °C) and Swabian Alb (384 °C) sites. The POM fraction had the

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highest CO₂ (477 °C), while rSOC had a first peak at 265 °C at both sites and a second peak at 392 °C for the Swabian Alb and 482 °C for the Kraichgau. The CO₂max was found to increase after 490 day incubation, while the C lost during incubation was derived from the whole temperature range but a relatively higher proportion from 200 to 350 °C. In situ₇ DRIFTS measurements indicated decreases in vibrational intensities in the order of C-OH = unknown C vibration < C-H < -COO/C = C < C = C with increasing temperature, but interpretation of vibrational changes was complicated by changes in the spectra (i.e. overall vibrational intensity increased with temperature increase) of the sample during heating. The relative quality changes and corresponding temperatures shown by the in situ₇ DRIFTS measurements enabled the fitting of four components or peaks to the evolved CO₂ thermogram from the FTIR-EGA measurements to have a semi-quantitative measure of the quality of evolved C during the heating experiment, lending more evidence that different qualities of SOM are being evolved at different temperatures from 200 to 700 °C. The CO₂max was influenced by long-term farmyard manure input and also by 490 days of laboratory incubation, indicating that this measurement can be an indicator for the relative overall SOM stability. The combination of FTIR-EGA and in situ₇ DRIFTS was shown to be useful for monitoring the rate of thermal decomposition of different soils and SOM fractions which were related to their relative stability. This knowledge was used for a peak fitting procedure for assigning proportions of evolved CO₂ to different thermal stability components.

1 Introduction

Various thermal analytical methods have been explored to study the quantity of soil organic matter (SOM) (Gaál et al., 1994) and its quality (Lopez-Capel et al., 2005). The basic hypothesis being that more labile OM such as carbon (C) associated with microbial biomass or light fraction C would also be thermally degraded at lower temperatures due to the lower activation energy needed to break the associated bonds, while more stable compounds would be evolved at higher temperatures. Thermal degradation

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remaining sample had undergone microbial mediated transformations; (ii) it is not well understood what changes a sample undergoes after being exposed to a thermal treatment and then cooled to room temperature to be analyzed for isotope composition, and (iii) very slow heating rates, as in the case of Dorodnikov et al. (2008, 2007) of $2^{\circ}\text{C min}^{-1}$, may shift thermal reactions to significantly lower temperatures (Fernández et al., 2011) and may possibly (v) lead to increased char formation as has been shown during combustion of cellulose (Baldry et al., 1988). Hence, an improved method to directly quantify thermal decomposition products and their quality would greatly advance the investigation of SOM via thermal analysis. To avoid the fore mentioned drawbacks of TGA/DTG and ex post facto analysis, on-line analyses such as FTIR-EGA (Fourier transform infrared-evolved gas analysis) and in situ₇ DRIFTS (in situ monitoring of thermal reactions via diffuse reflectance Fourier transform infrared spectroscopy) could be developed for monitoring thermal reactions of SOM (Plante et al., 2009). An online method provides the direct measurement of the combustion/decomposition products of thermal degradation of OM. FTIR-EGA has been used extensively for the rapid quantification of gaseous reaction products such as CO_2 , carbon monoxide, water, aliphatics and others for the analysis of lignite, chars of coal and spruce wood (Haselsteiner et al., 2011), and inorganic compounds (e.g. calcium carbonate, barium chloride, etc.) (Mittleman, 1990). This method relies on the vibrational frequencies of polar gas molecules in the mid-infrared range (4000 to 400 cm^{-1}) and it is usually the case that combustion products can be quantitatively determined by integrating the wavenumbers of the gas of interest (i.e. CO_2 at 2400 to 2200 cm^{-1}) and creating a calibration curve using a known standard (i.e. sodium bicarbonate) (Court and Sephton, 2009; Toops et al., 2005). The situ₇ DRIFTS method can be used to measure the changes in vibrational intensities at wavenumbers of interest of a sample during heating (Toops et al., 2005). Hence, combining FTIR-EGA and in situ₇ DRIFTS could have the potential for the rapid characterization of SOM based on the properties of the evolved gas profile (i.e. peak temperature, distribution of evolved gas) and the changes in vibrational intensity of mid-infrared wavenumbers during heating. In addition to quantifying the total

C amount in a soil sample, by optimizing the combustion conditions the distribution and peak temperature may be related to different chemical and or physical traits. This could then be linked to changes in vibrational frequencies of the soil at different temperatures during in situ DRIFTS measurements to unravel qualitative changes in the types of compounds undergoing thermal degradation.

The objectives of this study were to (i) develop improved experimental techniques of FTIR-EGA and in situ₇ DRIFTS systems for analyzing SOM in the range of C contents and stability found in bulk and SOM fractions, and (ii) to use these techniques to characterize SOM of different stabilities, treatments, and decompositional status. The hypothesis was that the characteristics of thermal CO₂ evolution (temperature of peak CO₂ evolution, changes in low temperature CO₂ evolution versus higher temperature CO₂ evolution) would be affected by different qualities of SOM. Soils and/or fractions which are more enriched in labile compounds (e.g. farmyard manure treated soil, POM) will have lower thermal stability as compared with soils and/or fractions which are more enriched in stable compounds (soil with long history of low residue return after harvest, silt + clay fraction, Lützwow et al., 2007, and/or a chemically resistant fraction, Zimmermann et al., 2007a).

2 Materials and methods

2.1 Soils

Soil samples were from three different sites in Germany. The first site was the Static Fertilization Experiment, Bad Lauchstädt, Germany (51.40° N, 11.88° E). Archive soil samples were taken from the years 1956, 1992, and 2004 of the treatments of farmyard manure, FYM (30 t ha⁻¹ every second year), and NPK fertilizer (123, 30 and 30 kg ha⁻¹ yr⁻¹ N, P and K, respectively), combination of both, FYM + NPK (30 t ha⁻¹ farmyard manure every second year and 103, 6 and 25 kg ha⁻¹ yr⁻¹ N, P and K, respectively as mineral fertilizers), and a control (CON) to examine how long-term fertilizer

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treatments affect SOM properties and thermal characteristics of the bulk soil. The experiment has been running since 1902 under a rotation of winter wheat, potatoes, spring barley, and sugar beets. Soil samples were taken in the fall following harvest of winter wheat from a depth of 0 to 30 cm. The soils were classified as Chernozems (IUSS Working Group WRB, 2007). More information about the experiment can be found in Körschens et al. (1994) and Table 1. The second study site (48.92° N, 8.70° E) was in the vicinity of Pforzheim, Germany in the Kraichgau region which is characterized by loess parent material and intensive agriculture. Soils sampled were classified as Cambisols (IUSS Working Group WRB, 2007). The third site (48.53° N, 9.77° E) was near the village of Nellingen, Germany in the Swabian Alb. The Swabian Alb soils were formed from limestone residuum and also classified as Cambisols (IUSS Working Group WRB, 2007). The crop rotation in the fields of both areas typically consists of winter wheat, maize, and oilseed rape. In both the Kraichgau and Swabian Alb sites two fields were selected with three plots each with a subplot sampled in the vegetation (winter wheat and maize in the Kraichgau, winter wheat and oil seed rape in the Swabian Alb) and a bare fallow subplot which was kept clear of vegetation during the experiment by hand pulling and periodic spot spraying of glyphosate. The fallow plots were used to investigate the turnover of SOM without fresh organic inputs such as roots, aboveground crop residues, and manure/slurry. Soil samples were taken one month after the establishment of the bare fallow subplots and in adjacent vegetated subplots at the end of May to beginning of June 2009. The Kraichgau and Swabian Alb sites were included as they are part of a larger regional climate change project as contrasting sites. The Kraichgau an example of a site with deep soils and milder climate, while the Swabian Alb a site with shallow soils and a harsher climate.

The mean annual precipitation and elevation gradients follow the order of Bad Lauchstädt (483 mm), Kraichgau (780 mm), Swabian Alb (962 mm) (Table 1a). Mean annual temperature is nearly the same in the Kraichgau and Bad Lauchstädt sites (9.1 and 8.8 °C, respectively), but more than two degrees lower in the Swabian Alb (6.7 °C).

The clay percentage was highest in soils of the Swabian Alb site (3%) and lowest in those of Kraichgau site (21 %).

2.2 Fractionation

Soil samples for fractionation (Kraichgau and Swabian Alb) and thermal analysis (all three sites) were air-dried and made to pass a 2 mm sieve. Visible roots and plant residues were removed prior to analysis. The fractionation method was modified from Zimmermann et al. (2007b). Briefly, 30 g of < 2 mm soil was made up to 150 ml with deionized water and sonified for two minutes at 30 J s^{-1} . The mixture was poured onto a $63 \mu\text{m}$ sieve and gently sieved until water passing through the sieve was clear. The < $63 \mu\text{m}$ portion was collected and dried at 40°C overnight to yield the silt and clay (Si + c) fraction. Before drying the bulk, moist Si + c fraction, 1 ml of 0.01 M calcium chloride solution for flocculation was added to a 20 ml subsample of the suspension and centrifuged for 15 min at $3000 \times g$. The clear supernatant was taken as extractible OC. The fraction remaining on the $63 \mu\text{m}$ sieve was transferred to a 10 ml test tube and 5 ml of 1.8 g cm^{-3} density sodium polytungstate (SPT) solution was added, mixed, and centrifuged for 15 min at $3000 \times g$. The fraction floating on top of the SPT was poured off and 4 ml SPT was added to the remaining fraction, mixed, and centrifuged again to remove any remaining light fraction material. The floating material yielded the particulate organic matter (POM) and the heavy material yielded the sand and > $63 \mu\text{m}$ stable aggregates (Sa + A) fraction. The separated fractions were rinsed with deionized water and dried at 40°C . A sub-sample of the silt and clay fraction was combined with 10 ml sodium hypochlorite and placed in a water bath at 95°C for 15 min (Anderson, 1963) to speed up the partial oxidation of the labile organic matter. The mixture was centrifuged for 8 min at $200 \times g$, decanted, and the oxidation, centrifugation, and decanting steps repeated twice. Finally, the residue was rinsed with deionized water and dried at 40°C to yield a resistant organic carbon (rSOC) fraction. Subsamples of each soil sample were fractionated twice.

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Total carbon (TC) of bulk soil and soil fractions were measured by dry combustion. Carbonate content of bulk soils was measured by the Scheibler method (Schlichting et al., 1995), while carbonates in the SOM fractions were destroyed by fumigation with hydrochloric acid (Harris et al., 2001). Bulk soils and fractions were then measured for TC by dry combustion with a Vario-EL III elemental analyzer (Elementar, Hanau, Germany).

2.3 Incubation experiment

Field moist samples from the Kraichgau and Swabian Alb site vegetated plots were sieved to < 4 mm and stored at 4 °C. One kg moist soil was transferred to 2.5 l glass jars and incubated in a dark, climate controlled room at 20 °C for 490 days. The lids to the jars were left slightly open to enable gas exchange, but to prevent rapid drying. Additionally, a 100 ml beaker of deionized water was placed in the jars for better moisture retention. Periodically, deionized water was added to the soils to keep the soil moisture content at 50 % of field capacity.

Additionally, at the beginning of the experiment, two 20 g moist weight replicates were taken from each field sample, sieved to 2 mm, adjusted to 50 % of field capacity and placed in a Respicond IV automated respirometer (Nordgren Instruments, Sweden) for the continuous measurement of CO₂ evolution during 44 days at 20 °C (the same temperature as the climate controlled room. At the end of the 44 day period, the incubation temperature was increased to 25 °C (standard temperature for microbial biomass determination) and, after stabilization of respiration, a 1 : 3 (*w* : *w*) glucose and talc mixture was added to measure (substrate-induced) microbial biomass (Anderson and Domsch, 1978). A pre-test was done with varying amounts of glucose mixture, with the maximum respiration response being with 0.16 g for Kraichgau and 0.32 g for Swabian Alb of the glucose mixture. The ratio of soil respiration rate measured on day 45 before addition of substrate to the microbial biomass (metabolic quotient – *q*CO₂ (Insam and Haselwandter, 1989) was used to estimate substrate use efficiency.

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2.4 FTIR-EGA method

2.4.1 Set up of FTIR-EGA thermal chamber

For measuring thermally evolved gases, a high temperature heating system was utilized in conjunction with a Bruker Tensor 27 (Bruker Optik GmbH, Ettlingen, Germany) infrared spectrometer. The high temperature reaction chamber (HTC) (Harrick Scientific Products, Pleasantville, NY, USA) had an integrated sample holder which could hold approximately 50–70 mg of soil sample and was equipped with a cartridge type heating element and a K-type thermocouple. The HTC was interfaced with an automatic temperature controller (Harrick Scientific Products, Pleasantville, NY, USA) with an integrated temperature/process controller (Watlow Winona, Minnesota, USA) for programmed heating rates and set-point temperatures. The HTC was closed by a gas tight dome with a high temperature O-ring. The dome had three windows, two made from potassium bromide to enable diffuse reflectance measurements (DRIFTS) of the soil, while the third window was made from quartz glass. The approximate internal volume of the heating chamber with installed dome was 20 ml. In the gas measurement mode (FTIR-EGA), the heating chamber was linked via a stainless steel Swagelok system (Swagelok-Stuttgart GmbH, Reutlingen, Germany) to a variable long path gas cell (Bruker Optik GmbH) which was placed in the accessory chamber of the Tensor 27 spectrometer (Fig. 1a). In the gas transfer line immediately after the heating chamber was a water trap of magnesium perchlorate and a sintered metal filter (2 μm) to prevent any particulate matter from reaching the gas cell and to act as a heat sink. The gas cell had a volume of 136 ml and a path length of 1 m.

Taking into consideration the range of C contents of the samples to be analyzed (0.13 to 48 %) for this study, the state conditions of purge flow rate, sample size, heating rate, infrared spectrometer scan rate, and mid-infrared wave number integration range were optimized (data not shown) to quantitatively determine the mid-infrared spectrometer signal response to total C amount, minimize secondary reactions, and to ensure similar heat transfer rates from the heating element to the sample as the

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shape and distribution of the evolved gas were to be used as additional parameters to link to SOM properties. After the pre-test the following procedure was adopted for the FTIR-EGA measurements. A scan was recorded every 4 s, with a resolution of 8 cm^{-1} . Synthetic air was used as the purge and carrier gas of the system with a flow rate of 15 l h^{-1} . The chamber was purged for 5 min after introducing the sample. Additionally, a baseline was taken before the beginning of each analysis in order to zero the signal in the gas cell. An optimized heating rate of $68\text{ }^{\circ}\text{C min}^{-1}$ (see section below) and set-point temperature of $700\text{ }^{\circ}\text{C}$ was used. The set-point temperature was reached after 10 min and held for another 20 min which resulted in a total of 400 individual FTIR scans. After pretesting in which it was found that CO_2 evolution ended after a shorter time duration, the final number of scans taken was reduced to 300 for a total analysis time of 20 min. The scans were then assembled into a single file or thermogram for further processing using the spectral processing software OPUS v 6.5 (Bruker Optik GmbH). The spectra were baseline corrected using the concave rubberband method with 64 baseline points and 10 iterations. Integration was performed on the baseline corrected spectra between 2400 to 2200 cm^{-1} , following Eq. (1):

$$\text{Area}_{\text{peak}} = \int_{2200\text{ cm}^{-1}}^{2400\text{ cm}^{-1}} A(\nu) \quad (1)$$

where $A(\nu)$ is the absorbance value of the investigated wavenumbers. The cumulative peak area was calculated by Eq. (2):

$$\text{Area}_{\text{cum}} = \sum_{j=1}^{300} j(\text{Area}_{\text{peak}}) \quad (2)$$

where j is the scan number which was taken every 4 s for a total of 300 scans and $j(\text{Area}_{\text{peak}})$ is the $\text{Area}_{\text{peak}}$ at scan j . The presence of a linear response of cumulative

peak area found by Eq. (2) to stoichiometrically calculated evolved CO₂ from a sodium bicarbonate standard was checked to establish a quantitative relationship.

In the present experiment lower heating rates were also tested (10 and 30 °C min⁻¹), but were found to result in an increase in the formation of secondary reaction products during heating as shown by other measurements (in situ DRIFTS), while heating rates > 68 °C resulted in non-linear increases in temperature and an overshoot of the final set point temperature. After the heating rate was set, the purge gas flow rate was adjusted in order that the maximum absorbance of the CO₂ peak (2400 to 2200 cm⁻¹) evolution was < 2.5 absorbance units (A.U.). If the absorbance is > 2.5 A.U. then there may not be a linear relationship between absorbance and the content of the compound of interest (Conzen, 2003). A relatively high purge rate of 15 l h⁻¹ was needed in order to minimize retention time in the gas cell, due to the large volume (136 ml). The scanning or wavenumber resolution of 8 cm⁻¹ was found adequate as the main gas of interest; CO₂ has a relatively broad spectral absorbance range (100 wave numbers) and does not require a very high resolution. The time in between each scan was first set at 40 s as this was the calculated time to purge the entire system, but was found to be too coarse a measurement interval especially for rapid increases in CO₂ evolution. A scan every 4 s gave a better time resolution of the rate of change with respect to time of CO₂ evolution. It was found that if any of these state variables were changed (purge rate, scan time, resolution, or heating rate), then a new calibration curve would need to be constructed to quantify CO₂ evolution.

Additionally, pure, reagent grade glucose (anhydrous, BDH Chemicals Ltd, Poole, UK), xylan (Sigma-Aldrich Chemie, Munich, Germany), and tannic acid (Carl Roth GmbH, Karlsruhe, Germany) were compared to gain information on the thermal decomposition/combustion behavior in the absence of any mineral influence. The substances were chosen as they vary in their chemical structure, ranging from a simple sugar in glucose to the more complex polyphenol type structure of tannic acid and to test the effect of a dilution with preheated quartz sand on CO₂ evolution to optimize combustion conditions.

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verified with the results from the in situ₇ DRIFTS given above to justify the presence of a specific component at a certain temperature. The residuals of the final fit were also inspected for normality and heteroscedasticity. A fitting procedure was considered completed when the $R^2 > 0.999$, $SE < 0.005$ and there was a homoscedasticity of residuals. The simplest fit (least number of peaks) was always considered the final solution. Initially, the peak fitting was repeated three times on the same sample to ensure stability or robustness of the fit and to determine if the fit was the most likely combination of solutions based on the data. Analysis of variance (significance at $P < 0.05$) was used to compare CO_2 max among the treatments at the Bad Lauchstädt site. A mixed modeling approached was used to compare the CO_2 max of the bulk soils and fractions in Kraichgau and Swabian Alb areas. The factors were site and fraction, with plot location as the random error.

3 Results

3.1 Soil characteristics

Results of C/N elemental analysis revealed that the soils of Swabian Alb and Bad Lauchstädt have nearly double the amount of total organic carbon content (1.94 and 1.85 %, respectively) compared to the Kraichgau site (0.94) (Table 1a). The contents of TOC and total nitrogen (TN) in the SOM fractions of Swabian Alb site were significantly higher ($P < 0.05$) in each fraction (Table 1b) compared to the Kraichgau with the exception of extractible SOM TN which was not different and rSOC TN which was below the analytical detection limit in the Kraichgau rSOC. Microbial biomass C as measured by the SIR method of incubated soils was more than twice as much in the Swabian Alb site (0.59 mg C g^{-1} soil) as compared to the Kraichgau site. The qCO_2 value was considerably higher ($P < 0.05$) at the Kraichgau site (11.8) than the Swabian Alb (3.6).

3.2 FTIR-EGA derived properties of organic substances and soils

In order to quantify evolved CO₂ from the thermal reactions, sodium bicarbonate was used as a standard due to its known stoichiometric thermal decomposition (Janković, 2009). An example of a single mid-infrared gas cell scan of evolved gas from NaHCO₃ decomposition can be found in Fig. 2, showing the three main vibrational modes of CO₂ at 2400–2200, 715–615, and 3760–3657 cm⁻¹ in order of decreasing intensity. Absorbance values of > 2.5 of the main CO₂ peak at 2400–2200 cm⁻¹ resulted in a non-linear response of Area_{cum} and calculated C evolved from the NaHCO₃ (data not shown). Thus, for the heating rate of 68 °C min⁻¹ and reaction chamber purge rate of 15 l h⁻¹, a C weight between 0.1–2.5 mg could be analyzed and result in a linear response ($R^2 = 0.99$) (Fig. 3). The three pure substances (glucose, xylan, and tannic acid) had very different FTIR-EGA CO₂ thermograms, such as number of peaks, peak position and general shape of the curve of CO₂ evolution (Fig. 4). In the undiluted samples (Fig. 4a) xylan was found to have the first CO₂ evolution peak at 320 °C, one at 500 °C, and the highest CO₂ temperature peak at 680 °C. Undiluted glucose had a prominent peak at 442 °C and a shoulder at 537 °C. The first two CO₂ peaks of undiluted tannic acid were present at 380 and 450 °C, and a final peak at 660 °C. To test if there was any effect on sample volume to FTIR-EGA derived thermal characteristics, a dilution of 1 : 100 with preheated quartz sand was done. This dilution resulted in relatively the same volume of heating chamber occupied compared with the bulk soils for the same quantity of organic carbon. The dilution resulted in shifts of the peak temperatures and also the peak heights relative to C content. Xylan still had the earliest CO₂ peak, but was shifted to a higher temperature at 346 °C and a second peak at 518 °C. Glucose had only one CO₂ peak at 380 °C. Tannic acid had two poorly resolved peaks, one at 410 °C and a final peak around 577 °C. As a percentage of total evolved C, 80 % was recovered upon reaching 700 °C (10 min) from undiluted samples, while in the diluted samples, 90 % was recovered.

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Due to the large range in C contents of samples analyzed (0.1 to 48% OC), the sample weight was adjusted to fit into a range from 0.1 to 2.5 mg OC content in order to stay within the linear range of the calibration curve (Fig. 3). In the case of POM, which had between 26–32% C by weight, the above C content would only result in a maximum sample weight of 6 mg as compared to 30 to 50 mg of the other fractions and bulk soil. Thus, due to the small sample weight and the small volume occupied within the heating chamber, a 1 : 50 dilution was made with ball-milled quartz sand, which had previously been heated to 600 °C to remove any C impurities. This dilution ratio was used to gain roughly the same volume of material as was analyzed with the bulk soil and lower C content fractions and to result in C amounts between the 0.1 to 2.5 mg range.

3.3 FTIR-EGA derived properties of soils and fractions

The CO₂max evolution was influenced both by long-term fertilizer application in the case of the Bad Lauchstädt soils (Table 2) and also when comparing by site (Bad Lauchstädt, Kraichgau, Swabian Alb). In the Bad Lauchstädt soils the CO₂max increased from 419 °C in the FYM+NPK treatment to 428 °C in FYM and 473 °C in the NPK and Control soils. Compared to the TOC contents which were only significantly affected by FYM application, the FTIR-EGA method also indicated a difference between the FYM + NPK and FYM treatments. When comparing soils from the three sites (Fig. 5), the peak CO₂ evolution not only had different maximum heights for the three soils, but also different temperatures. The average for the Swabian Alb site soils had the lowest CO₂max at 384 °C, while that of the Kraichgau soils was at a significantly higher ($P < 0.05$) temperature (392 °C). The CO₂max average of all Bad Lauchstädt samples was much later at 447 °C, even factoring in the effect of long-term manure treatment. The CO₂ thermogram also revealed that while the Kraichgau and Swabian Alb soils had a similar CO₂ evolution pattern with a rapid increase in CO₂ evolution between 275 to 380 °C, the Bad Lauchstädt soils had a much broader peak covering a range of approximately 80 °C.

The temperature of the individual CO₂ evolution peaks of SOM fractions separated from the bulk soil of the Kraichgau and Swabian Alb sites were generally found to be the same among the sites, with the exception of the second peak of rSOC fraction, which was much higher at the Kraichgau site (482 °C) compared to the Swabian Alb site (392 °C) (Table 3). The largest differences in relation to the bulk soil were the rSOC fractions, which had two well defined peaks and the POM, which had a first poorly defined peak or “shoulder” around 380 °C, the same temperature as the bulk soil, but then a main peak much later compared to the bulk soil at 477 °C.

Soils measured after incubation for 490 days showed a decrease in thermally evolved CO₂ (Fig. 6) and a shift in the CO₂. The difference CO₂ thermograms (Fig. 6c) taken by subtracting the two thermograms show from which temperature regions C has been released during the long-term incubation. The maximum difference between pre- and post-incubation evolved CO₂ was at 360 and 378 °C for the Kraichgau and Swabian Alb, respectively, with CO₂ shifted to a slightly higher temperature (increase of 4 °C).

3.4 In situ_T DRIFTS

In situ_T thermal DRIFTS measurements showed changing vibrational intensities which depended on the heating chamber temperature and the functional groups being studied. The lowest temperature of a vibrational change was from 80 to 200 °C which was a rapid decrease in the O-H vibration at 3600 cm⁻¹ (data not shown) indicating water loss. Thus, subsequent changes in vibrational intensities were related to the base at 200 °C as changes from water loss were apparently largely finished and CO₂ evolution as measured by FTIR-EGA began after 200 °C. Certain organic functional group associated vibrations (i.e. aliphatic, carboxylate, aromatic) differed in their temperature sensitivity shown by specific temperature ranges of changing vibrational intensity (Fig. 7). The temperature range between 220 to 300 °C was associated with a slight decrease of C-O/C-OH vibrations and a larger decrease of C-H and “other” vibrations. These “other” vibrations (at 692 cm⁻¹) seemed to be an organic functional group as there was a decrease in intensity during heating, but it was unclear from literature as to which

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organic functional group it could be assigned. Between 300 to 370 °C, there was a continued decline of the “other” vibrations and a drastic decrease in C-H vibrations while at the same temperature range a slight increase in C = C/-COO vibrations and a stronger increase in C = C vibrations. Interestingly, after a slight decline up to 330 °C, the C-OH vibrations increased rapidly to a maximum intensity around 500 °C. At approximately 400 °C, the C = C/-COO vibrations decreased and after 430 °C the C = C vibrations decreased. Vibration intensities of wavenumbers below 1000 cm⁻¹ were rather difficult to interpret (data not shown) due to the lack of clear trends, high variation from one scan to the next, and absorbance values of > 2.5 A.U. especially at temperatures > 500 °C.

3.5 Peak fitting of FTIR-EGA CO₂ gas thermograms

With the temperatures of maximum change of different functional groups as measured by in situ₇-DRIFTS analyses as a guideline, a peak fitting of the FTIR-EGA CO₂ gas profiles from bulk soils resulted in four different peaks or “fitted components” (Table 4). As with the measured CO₂max, the maximum of each fitted component was at a slightly lower temperature in the Swabian Alb compared to the Kraichgau. The 1st component had a peak center at almost the same temperature in both soils (Kraichgau 290 °C, Swabian Alb 289 °C), but there was a larger difference in the second and third components. Component 2 in the Kraichgau had a peak center at 353 °C compared to 344 °C in the Swabian Alb, while that of the 3rd component was at 445 °C in the Kraichgau compared to 432 °C in the Swabian Alb. Again a similar but smaller difference was found for the 4th component with its center at 549 °C in the Kraichgau soils compared to 541 °C in the Swabian Alb soils. The largest contribution to the total CO₂ evolution was provided by component 2 (35–46 %) for both soils. The 1st component was the smallest fraction, being slightly higher in Swabian Alb soils (4.7 %) compared to Kraichgau (3.4 %). Larger differences between sites were found for components 2 and 3 with 46 and 27.3 % for the Kraichgau and 35 and 34 % for the Swabian Alb. Lastly the 4th component was larger in the Swabian Alb at 26 % compared to 23 % in the Kraichgau.

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4 Discussion

4.1 Thermal stability of organic matter of soils and fractions

Our results confirmed the hypothesis that an optimized FTIR-EGA analysis is sensitive to changes in the quality and composition of organic matter and that the evolved CO₂ profile indicates a clear link between thermal stability and soil functions. Using the temperature of peak CO₂ evolution as one indicator of thermal stability, the results from the three contrasting soils indicate that there may be a large portion of stable OM present in the Bad Lauchstädt soils. These findings are in agreement with what others have found during previous analyses of soils from Bad Lauchstädt by DTA, TGA (Leifeld et al., 2006), and pyrolysis-field ionization mass spectrometry methods (Leinweber and Schulten, 1993) and which may be due to the presence of very stable humus compounds formed within a Chernozem or the presence of black C (Eckmeier et al., 2007). The effect of long-term manure application was evident in the FYM + NPK and FYM treatments of the Bad Lauchstädt soils with a relative enrichment of thermally labile substances as indicated as a lower temperature of CO₂max. It has also been shown that in the control treatment relative to the FYM + NPK treatment a relative enrichment of C in the clay, heavy density fractions, and of aromatic functional groups in the bulk soil via specific DRIFTS peak areas at the expense of the more labile fractions (Demyan, et al., 2012).

Further evidence of a link between FTIR-EGA results and soil functional properties were provided by the laboratory incubation study, which confirmed that ongoing microbial decomposition alters the thermal CO₂ thermogram of the remaining SOM. Although, after a 490 day laboratory incubation experiment, the quality of lost C spanned the entire range of thermal stabilities, the maximum peak of C lost during incubation was slightly lower than the unincubated soil CO₂max. This indicates that the possible source of a large part of the respired C during incubation came from the Si + C fraction, which was also the largest fraction by weight in the bulk soil, and also had a similar peak temperature as compared with the bulk soil. While the effect of the 490 day incubation

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did shift the CO_2 max to a slightly higher temperature, the C loss was not confined to lower temperatures (below 350°C), but was also evolved at higher temperatures indicating some apparently labile compounds easily decomposable to microorganisms are quite thermally resistant as shown for the pure substances. Plante et al. (2011) also found that soils incubated for 588 days at 35°C have a higher thermal stability as indicated by the temperature at which 50 % of the mass loss or energy loss occurred measured via TG/DSC. Using this same 50 % threshold, but with evolved CO_2 via FTIR-EGA, our results showed an increase from 433 to 442°C after incubation. From these results, we can conclude that both CO_2 max and 50 % evolved C loss as measured by FTIR-EGA seems to be an indicator of the relative stability of SOM in these soils.

The thermal stability gradient of the SOM fractions did only partially follow their implied stabilities. There was a gradient in the mineral associated fractions going from less to more thermal stability in the order $\text{Sa} + \text{A} < \text{bulk soil} < \text{Si} + \text{C}$ but CO_2 was not significantly different ($P < 0.05$). The non-mineral associated POM did not fit into this relationship, as it had a higher peak temperature compared to the $\text{Sa} + \text{A}$, $\text{Si} + \text{C}$ and bulk soil, but this comparison may not be straightforward as it was shown in this study that dilution with quartz sand could change the CO_2 max of POM. This could also suggest that a portion of this fraction is relatively undecomposed, which has not been subject to microbial decomposition (Schulten, 2009) and has relatively intact plant parts. As was shown with the pure substances in our study, a high thermal stability was also found for components within xylan and tannic acid which would also be present in the form of hemicelluloses and polyphenols/lignins in the relatively undecomposed plant residues having lost its labile compounds prior to sampling which make up this POM. Others have also shown that there is a resistant POM fraction as based on the size separation of $> 100 \mu\text{m}$ of $< 1.8 \text{ g cm}^{-3}$ being more labile and 100 to $53 \mu\text{m}$ of $< 1.8 \text{ g cm}^{-3}$ being more stable (Cadisch et al., 1996).

4.2 Allocation of thermally evolved carbon

Using a novel approach of a peak fitting procedure we were able to identify different “pools” of SOM with characteristic thermal signatures. This might lend evidence to link with functional properties such as used in SOM decomposition models. Through the peak fitting procedure, C, as measured by the FTIR-EGA, was allocated into several peaks or fitted components. Using the least squares iterative peak fitting procedure resulted in significant ($R^2 > 0.999$, standard error < 0.005 , $P < 0.05$) and reproducible fits to the measured data. Additional support for the results were that the centroid or maximum of each fitted peak was consistent among the two sites and that these peaks coincided with different maximum or near maximum decreases in vibrational absorbances as measured by in situ₇ DRIFTS of a first slight decline in C-O, C-OH, and C-H vibrations, then a strong decrease in C-H and continued decline in C-O vibrations and finally a decline in C=C, which lends evidence to different organic compounds being decomposed at different temperatures. Kiem et al. (2000) found a similar stability or depletion sequence in comparisons of long term managed fallow treatments compared with fertilized treatments using ¹³C nuclear magnetic resonance and carbohydrate analysis. Additionally via pyrolysis field ionization mass spectroscopy, Sleutel et al. (2011) have shown that at $< 400^\circ\text{C}$ combustion products being enriched in lipids, carbohydrates, and peptides compared to $> 400^\circ\text{C}$ where there was a greater proportion of alkyl-aromatics. In the current study the larger percentage of fitted component 1 in the Swabian Alb compared to the Kraichgau corresponds to the larger microbial biomass of the Swabian Alb. Additionally the larger percentage in the most thermally stable component, the 4th, in the Swabian Alb may have been a result of the higher clay content of the Swabian Alb compared to the Kraichgau soils. The degree of protection may also be reflected in the physiological difference of the microbial biomass, as the higher $q\text{CO}_2$ of the Kraichgau site measured during the incubation experiment may indicate a microbial population which is less protected compared to the Swabian Alb site, thus less efficient and more stressed. Further vibrational functional groups may be of

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interest and related to OM, but in our study it was found that the absorbance values of the wavenumbers $< 1000 \text{ cm}^{-1}$ where there is a strong influence of mineral vibrations (Nguyen et al., 1991), increased during the entire heating procedure or were highly variable from one scan to the next, complicating interpretation. As the studied vibrational frequencies were selected based on the fact that they represent mostly organic and not mineral functional groups (Demyan et al., 2012), any changes in absorbance intensity due to mineralogical changes especially $> 540^\circ\text{C}$ should have been avoided. This combined use of both in situ DRIFTS and FTIR-EGA information to assign evolved CO_2 of different temperature intervals to different qualities of organic matter may be a promising and new step towards application of this method.

4.3 Specific considerations using FTIR-EGA thermal approaches

Several conditions must be met to obtain satisfactory FTIR-EGA results.

First, a major drawback in oxidative thermal combustion reactions is the potential of formation of secondary reactions, e.g. charring, during the heating process. It is thus important to set up experimental conditions with minimal interference from such secondary reactions. Our tests showed that low heating rates favored formation of secondary reactions. We therefore identified $68^\circ\text{C min}^{-1}$ as the optimal heating rate for soils for our system to balance the need for reproducible heating rate and minimizing secondary reactions. This heating rate is similar to the $70^\circ\text{C min}^{-1}$ used in pyrolysis-field ionization mass spectrometry (Py-FIMS) experiments by Schulten and Leinweber (1993). This may also have led to the occurrence of only one CO_2 peak for the bulk soils as opposed to traditional TGA or DSC profiles which even for bulk soils usually show two distinct peaks of OM associated weight loss (Dell'Abate et al., 2003). A possible reason for the lack of additional peaks is that we used a much higher heating rate ($68^\circ\text{C min}^{-1}$) compared to other studies (Siewert, 2004; Plante et al., 2011; Leinweber et al., 1992) which used a rate of $10\text{--}30^\circ\text{C min}^{-1}$ and may be subject to more charring effects.

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Secondly, the amount of potential CO₂ evolution will determine the experimental conditions used during analysis. In our case a C content of >2.5 mg in the sample cup resulted in absorbances of > 2.5 A.U. which were no longer linear in respect to C concentration.

Thirdly, the combustion conditions should be similar among the tested materials. This is particularly true for material with high organic carbon content. Thus with POM and the organic standards (glucose, xylan, tannic acid) the CO₂ evolution profiles changed by diluting a sample with pre-heated quartz sand. This may have to do with increasing the aeration within the sample and also changing its heat conductivity compared to a pure sample. It has been suggested that secondary reactions such as charring are present during combustion of cellulose, hemicellulose, and tannic acid (Court et al., 2009). As these secondary reactions do not necessarily reflect the thermal stability of the compound, but are rather a result of the heating procedure, care must be taken in interpreting the thermal characteristics of high OC content substances. For the current experimental setup, we propose that for non-mineral samples (POM, organic soils, plant samples) that a dilution with inert material (quartz sand) may be beneficial in replicating the thermal conditions of mineral soils and fractions which will reduce charring and standardize the aeration and thermal conductivity of the sample which is important at high heating rates.

4.4 Effect of sodium hypochlorite on thermal characteristics

Sodium hypochlorite is normally used to efficiently remove OM from soils and clays without greatly altering the clay mineral structure (Mikutta et al., 2005). Depending on the reaction conditions and time, a large portion of the OM is removed while the remaining portion is called a recalcitrant pool (Zimmermann et al., 2007b). Our FTIR-EGA results indicated that the NaOCl treatment has greatly altered the nature of the Si + C fraction as measured on the remaining residue (rSOC) so that there was a much less thermally stable peak evolved at relatively low temperature. The sodium saturation of the clay minerals has resulted in an increase of the thermal lability of a portion of

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the remaining OM. This seemed to be the effect of the complete dispersion of any microaggregates and also exchange of organic substances from the clay minerals. It was surprising that this relatively thermally labile pool has survived oxidation by the sodium hypochlorite, which may be because NaOCl does not completely attack aliphatic C compounds (Sleutel et al., 2009), which has been shown to have a lower thermal stability, as compared to aromatic C (Schulten and Leinweber, 1999) and seems to lend evidence that physiochemical protection is playing a role in influencing the thermal stability of the Si + C fraction. This was also shown qualitatively in our in situ₇DRIFTS measurements of the bulk soils in which C-H vibrations decreased rather rapidly and at an earlier temperature compared to C = C vibrations. As the rSOC fraction was very low in C content (0.1 to 0.2% by weight), in situ₇ DRIFTS did not yield much information for spectral changes due to the fact that background noise was higher than organic functional group absorbance changes. Due to the evident chemical alteration of the rSOC fraction by the NaOCl oxidation that has been used to isolate a supposedly very stable fraction, the thermal properties are greatly altered and this fraction may not be suitable for analysis by FTIR-EGA to infer biological stability.

5 Conclusions

The linking of a high temperature thermal reaction chamber with a FTIR gas cell was shown to be able to quantify evolved gas CO₂ in order to characterize SOM of different soils and SOM fractions. The peak temperatures and peak shapes of the thermograms of bulk soils were found to differ by long-term fertilization management (Bad Lauchstädt), soil type (Bad Lauchstädt, Kraichgau, Swabian Alb), and after a long-term (490 days) incubation. Temperature of maximum CO₂ evolution was shown to decrease with application of farmyard manure and found to increase after incubating soils for 490 days indicating that the temperature of maximum CO₂ evolution could be used as an indicator of the relative stability of SOM. SOM fractions were also found to vary in thermal characteristics, which in the mineral fractions, seemed to coincide

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with their quality or relative stability, apart from rSOC due to its altered properties during the oxidation with NaOCl. The conditions for an optimized FTIR-EGA procedure were (1) the use of a standard with well known thermal decomposition reaction (i.e. NaHCO₃) to quantify mid-infrared absorbance units to CO₂ production and to identify the optimal purge and scan rates which for our 136 ml gas cell were 15 l h⁻¹ synthetic air purge with a scan every 4 s, (2) a rapid heating rate (68 °C min⁻¹) to minimize char formation, and (3) a dilution of high carbon content samples, especially POM and plant samples for similar heating conditions in the heating chamber as compared to mineral soils.

A peak fitting procedure was used to allocate C evolved at different temperature into separate peaks. Results with the in situ₇ DRIFTS measurements gave evidence of different C components (i.e. C-OH = unknown C vibration <C-H <-COO and C = C < C = C) being evolved at different times during the 220 to 700 °C which justified and lent a quality aspect to the curve fitting procedure for the FTIR-EGA evolved CO₂. A combination of the FTIR-EGA and in situ₇DRIFTS methods may provide an improved approach for SOM characterization. Analysis of soils with different clay mineralogies and land use types is needed to test the applicability of this method to different soils and land uses.

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Table 1a. Study site characteristics.

| Study Site | Location | MAP ¹ /mm | MAT ² /°C | Soil type | Elevation/mASL ³ | TOC ⁴ /% | Clay/% |
|----------------|-----------------------|----------------------|----------------------|-------------------|-----------------------------|---------------------|--------|
| Bad Lauchstädt | 51°24′ N, 11°53′ E | 483 | 8.8 | Haplic Chernozem | 113 | 1.85 | 21 |
| Kraichgau | 48°54′ N, 8°42′ E | 780 | 9.1 | cambisol/ regosol | 276 | 0.94 | 11 |
| Swabian Alb | 48°30′ N, 9°42′ E | 962 | 6.7 | Cambisol | 640 | 1.94 | 30 |

¹ Mean annual precipitation, ² mean annual temperature, ³ meters above sea level, ⁴ by C/N elemental analyzer.

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Table 1b. Mean values (\pm standard errors) of organic carbon (OC) and total nitrogen (TN) of bulk soil and fractions from the sites Kraichgau and Swabian Alb based on oven dried (105 °C) basis.

| Soil parameter ¹ | Site | | | |
|-------------------------------|-------------------------|-------------------------|-----------------------|-----------------------|
| | Kraichgau | | Swabian Alb | |
| | OC/mg g ⁻¹ * | TN/mg g ⁻¹ * | OC/mg g ⁻¹ | TN/mg g ⁻¹ |
| Bulk soil | 9.40 (0.18) | 0.81 (0.03) | 19.40 (0.57) | 1.85 (0.07) |
| Extractible SOM | 0.14 (0.06) | 0.10 (0.01) | 0.38 (0.02) | 0.11 (0.01) |
| POM | 0.84 (0.07) | 0.05 (0.00) | 1.34 (0.14) | 0.09 (0.01) |
| Sa + A | 0.42 (0.02) | 0.04 (0.00) | 0.63 (0.09) | 0.06 (0.01) |
| Si + C | 7.92 (0.14) | 1.02 (0.02) | 13.31 (0.59) | 1.41 (0.06) |
| rSOC | 1.38 (0.05) | NA ² | 2.94 (0.24) | 0.19 (0.01) |
| C _{mic} | 0.24 (0.04) | ND ³ | 0.59 (0.07) | ND |
| qCO ₂ ⁴ | 11.8 (2.2) | ND | 3.6 (0.4) | ND |

* mg OC g⁻¹ bulk soil by C/N elemental analyzer.

¹ Bulk soil < 2 mm, Extractible SOM-dissolved SOM captured during wet sieving of silt and clay from sand and stable aggregates, POM-sand fraction < 1.8 g cm⁻³, S + A sand fraction > 1.8 g cm⁻³, silt + clay < 63 μm, rSOC < 63 μm treated with hot sodium hypochlorite, C_{mic}-microbial biomass as measured by substrate induced respiration method (Andersen and Domsch, 1993), ² values below detection limit, ³ not determined, ⁴ qCO₂-metabolic quotient of basal respiration as averaged over 10 h before addition of glucose divided by microbial biomass C as measured by SIR method.



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Table 2. Average (years 1956, 1992, 2004) total organic carbon (TOC) in bulk soil and FTIR-EGA measured peak temperature of CO₂ evolution during heating from 25 to 700 °C of soils from the Static Fertilization Experiment, Bad Lauchstädt. Values in parentheses are standard errors. Different letters within each column indicate a significant difference ($P < 0.05$) among the four treatments.

| Treatment | TOC/% | Peak Temperature/°C |
|------------|---------------|---------------------|
| FYM + NPK* | 2.21 (0.11) a | 419 (3) a |
| FYM | 2.04 (0.08) a | 428 (2) b |
| NPK | 1.65 (0.03) b | 473 (2) c |
| Control | 1.48 (0.03) b | 473 (2) c |

* FYM + NPK (farmyard manure and mineral fertilizer), FYM (farmyard manure), NPK (mineral fertilizer), Control (no fertilizer inputs).

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Table 3. Mean values (\pm standard error) by soil (Kraichgau and Swabian Alb) of the temperatures ($^{\circ}$ C) of peaks or “shoulders” of thermally evolved CO_2 of bulk soil and SOM fractions as measured by FTIR-EGA. Lower case letters indicate significant differences ($P < 0.05$) between peak temperatures in a row (among the sites), different letters indicate significant differences ($P < 0.05$) within a site, among fractions.

| Fraction | site | | | | | |
|------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| | Kraichgau | | | Swabian Alb | | |
| | 200–350 $^{\circ}$ C | 350–450 $^{\circ}$ C | 450–550 $^{\circ}$ C | 200–350 $^{\circ}$ C | 350–450 $^{\circ}$ C | 450–550 $^{\circ}$ C |
| bulk soil ¹ | | 392 (2) Aa | | | 384 (2) Ab | |
| POM ¹ | | | 477 (5) B | | | 476 (6) B |
| S + A ¹ | | 362 (1) A | | | 369 (7) A | |
| silt + clay | | 400 (1) A | | | 399 (4) A | |
| rSOC ¹ | 265 (1) D | | 482 (17) BDa | 265 (5) D | | 392 (15) BDb |

¹ Bulk soil < 2 mm, POM-sand fraction < 1.8 g cm⁻³, S + A sand fraction > 1.8 g cm⁻³, silt + clay < 63 μ m, rSOC < 63 μ m treated with hot sodium hypochlorite. ² Indicates that a peak was not present in these temperature regions.

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Table 4. Temperature and relative contribution to total evolved CO₂ of fitted peaks/components (\pm standard errors) from an iterative least squares approach of thermally evolved CO₂ from 25 to 700 °C (68 °C min⁻¹ heating rate) as measured by FTIR-EGA. Peak temperatures of the components were derived from relative changes of vibrational intensity of organic functional groups by in situ_T DRIFTS.

| Site | Component 1 | | Component 2 | | Component 3 | | Component 4 | |
|-------------|-------------|-----------|-------------|------------|-------------|------------|-------------|------------|
| | Temp/°C | %* | Temp/°C | % | Temp/°C | % | Temp/°C | % |
| Kraichgau | 290 (2) | 3.4 (0.2) | 353 (1) | 46.1 (0.6) | 445 (1) | 27.3 (0.4) | 549 (2) | 23.3 (0.6) |
| Swabian Alb | 289 (2) | 4.7 (0.3) | 344 (1) | 35.3 (1.0) | 432 (2) | 33.9 (0.7) | 541 (2) | 26.1 (0.9) |

* Percent contribution of component to total evolved CO₂.

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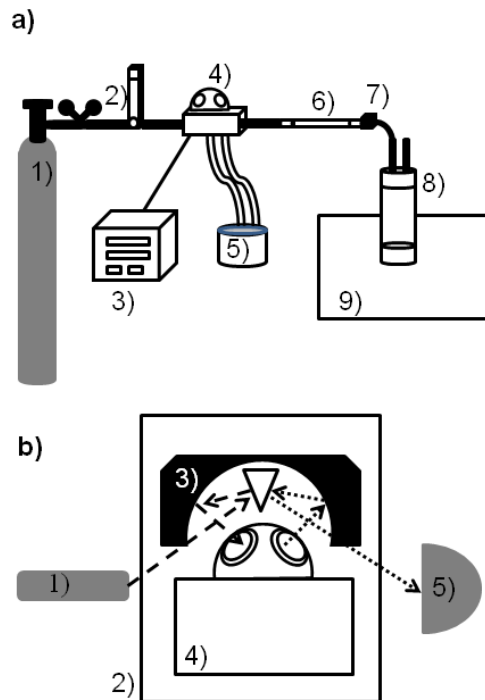


Fig. 1. Schematic of experimental setups. **(a)** FTIR-EGA system: (1) synthetic air purge/carrier gas, (2) pressure regulator and flow gauge, (3) automatic temperature controller, (4) high temperature reaction chamber with potassium bromide (KBr) windows and integrated sample cup, (5) recirculating cooling water, (6) glass tube with magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) water trap, (7) sintered metal particulate trap, (8) variable path length gas cell, (9) FTIR spectrometer. **(b)** In situ DRIFTS system: (1) infrared source, (2) diffuse reflectance chamber, (3) globular mirror, (4) high temperature reaction chamber with potassium bromide (KBr) windows and integrated sample cup, (5) detector. Dashed lines indicate source infrared beam, dotted lines indicate diffusely reflected infrared beam.

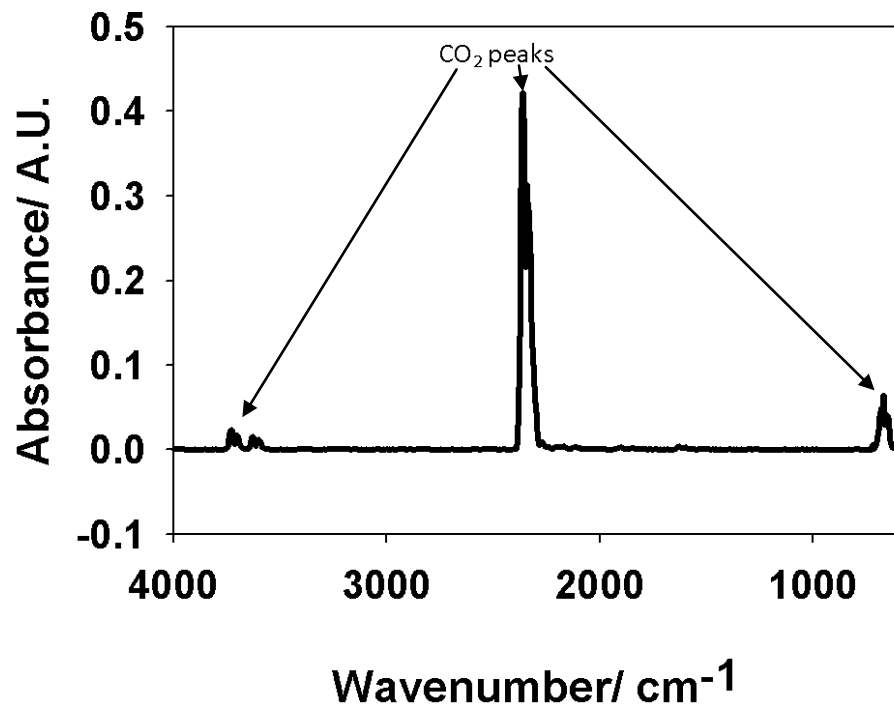


Fig. 2. Single scan of online evolved gas as measured by the FTIR-EGA system, with corresponding CO₂ peaks.

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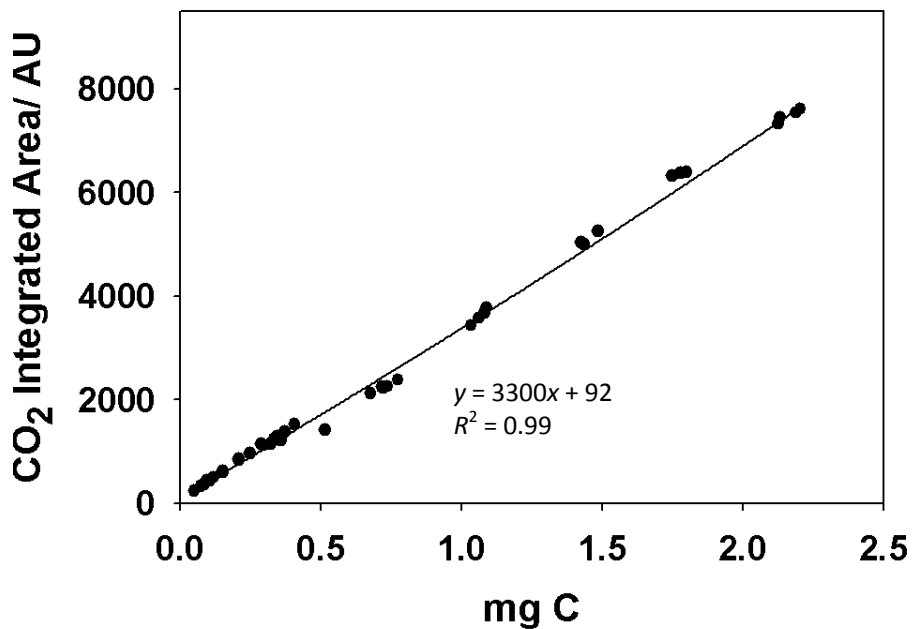


Fig. 3. CO₂ calibration curve of the FTIR-EGA with NaHCO₃.

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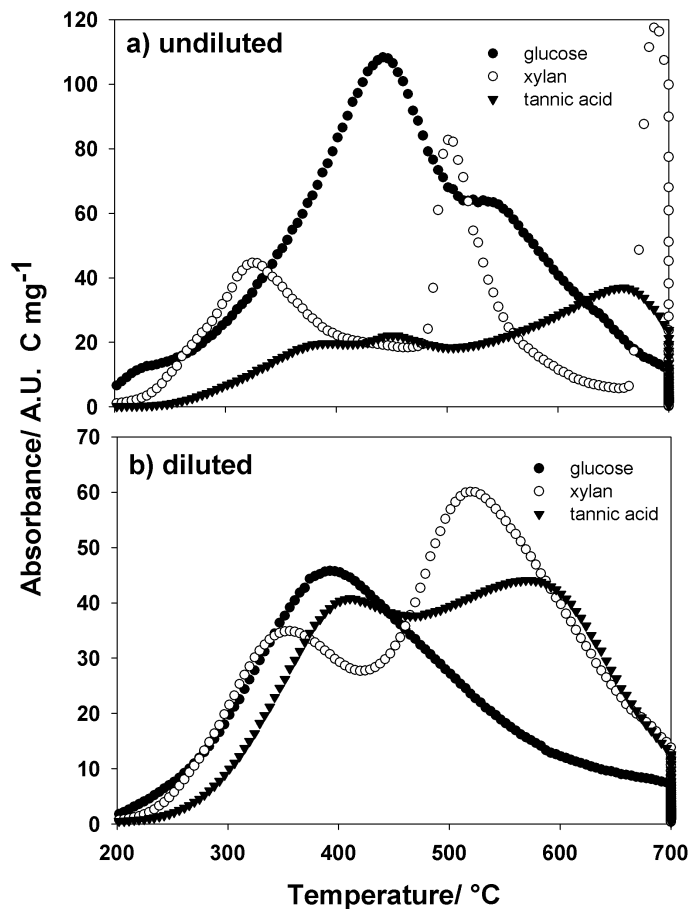


Fig. 4. FTIR-EGA thermograms of three selected substances. **(a)** Neat samples, **(b)** diluted 1 : 100 with preheated, ball-milled quartz sand.

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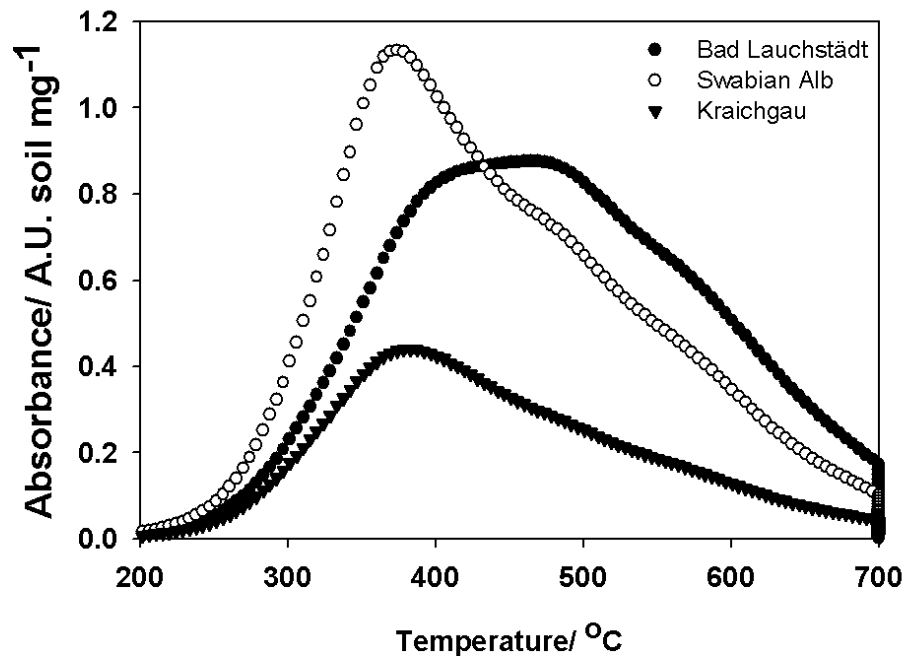


Fig. 5. FTIR-EGA average CO₂ thermograms of soils from three different agroecological sites (Bad Lauchstädt, Kraichgau, Swabian Alb).

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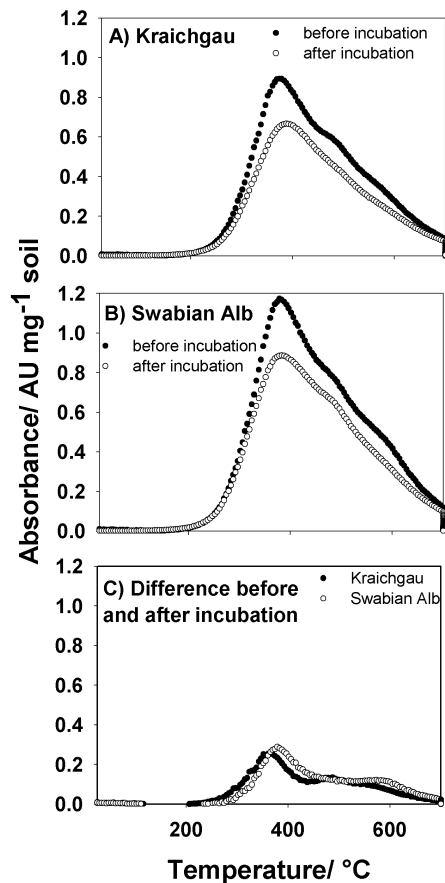


Fig. 6. Effects of 490 day incubation on thermally evolved CO₂ thermogram. **(a)** Kraichgau soils, **(b)** Swabian soils, **(c)** difference when subtracting thermogram of soil at beginning of incubation from thermogram at the end of the incubation.

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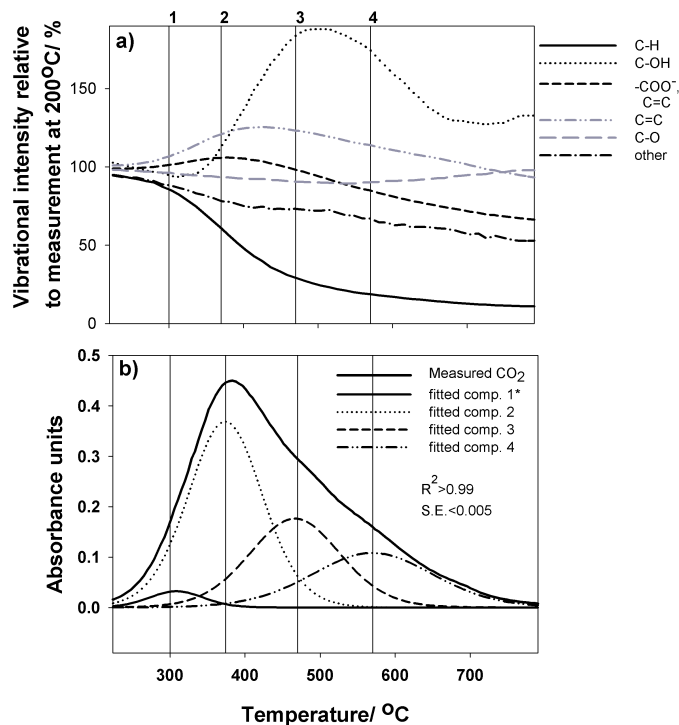


Fig. 7. Qualitative changes in organic functional groups during heating as a guide to fitting components to quantitative evolved gas analysis: **(a)** in situ₇ DRIFTS measurements of bulk soil from the Kraichgau site as a percentage of the vibrational intensity at 200°C to identify temperature of maximum change of functional groups. **(b)** Peak fitting with four components of evolved gas profile as measured by FTIR-EGA of bulk soil from Kraichgau site using previously identified temperatures of maximum change of functional groups. Statistics are from the goodness of fit of the four fitted components to the measured data. Reference lines 1 to 4 indicate the peak of the fitted components of the FTIR-EGA gas profile in Fig. 7b (* fitted component).