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Interrelations between soil respiration and its thermal stability

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Abstract Biological transformation of organic matter in soil is a crucial factor affecting the global carbon cycle. In order to understand these complex processes, soils must be investigated by a combination of various methods. This study compares the dynamics of biological mineralization of soil organic matter (SOM) determined via CO_2 evolution during an 80-day laboratory incubation with their thermo-oxidative stability determined by thermogravimetry (TG). Thirty-three soil samples, originating from a wide range of geological and vegetation conditions from various German national parks were studied. The results showed a correlation between the amount and rate of respired CO_2 and thermal mass losses of air-dried, conditioned soils occurring around 100 °C with linear coefficients of determination up to $R^2 = 0.85$. Further, correlation of soil respiration with thermal mass losses around 260 °C confirmed previous observations. The comparison of TG profiles from incubated and non-incubated soils underlined the importance of thermal mass losses in these two temperature intervals. Incubated soils had reduced thermal mass losses above 240 °C and conversely an increased mass loss at 100–120 °C. Furthermore, the accurate determination of soil properties by TG such as soil organic carbon content was confirmed, and it was shown that it can be applied to a wider range of carbon contents as was previously thought. It was concluded that results of thermal analysis could be a helpful starting point for estimation of soil respiration and for development of methods revealing processes in soils.

Keywords Soil respiration · Thermogravimetry · Prediction

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Introduction

Soil organic carbon (SOC) is a crucial factor in global carbon cycling and land use development under changing climatic conditions. However, the complexity of biological transformation processes is not yet fully understood. The availability of relevant data is hampered by the complex network of interactions between soil formation factors (parent material, climate, vegetation, fauna, etc.), and soil biology. However, such basic data are necessary to model the carbon cycle and to understand long term changes in the biosphere [1, 2].

Thermo-analytical techniques represent a simple tool for the investigation of soil physical and chemical properties. Examples from the literature show promising applications of thermal analysis in soil and environmental sciences [3–8]. For example, recent results indicate the possibility of rapid determination of basic soil properties using thermogravimetric analysis (TG) [6]. Using thermal mass losses in predefined temperature intervals instead of usual statistical peaks analyses, the content of carbon (C), nitrogen (N),

clay, and carbonates can be estimated in soils with the accuracy comparable to elemental analyses. This time and money-saving approach uses narrow 10 °C temperature intervals and, respectively, very small parts of soil organic matter (SOM) losses for the accurate determination of the SOC content. Although this method can be used only for soils not for carbon-containing mineral substrates, such correlation implies interconnections between long-term biological processes determining carbon content in soils and their thermal properties.

Soil incubation experiments represent a common tool to evaluate biological processes. In such experiments, biological activity is usually assessed by the measurement of CO_2 evolution, O_2 consumption, enzyme activity, or other parameters. In combination with physical and/or chemical characterization of soil properties, such experiments are very helpful to study the soil regulation processes and their mechanisms [1, 9, 10]. On the contrary, incubation methods are usually time consuming, sometimes sensitive to the experimental conditions and sample origin and do not give information about the quality of substances involved in the transformation processes. Therefore, these methods should be combined with other methods to shed light on the complex transformation processes in soils and their dependencies on environmental conditions.

The aim of this study was to verify a connection between thermal stability of soils detected via TG. For this purpose, this study compared thermal mass losses from TG of air-dried soil samples with the results of CO_2 evolution resulting from the microbiological transformation of SOM.

Materials and methods

Soil samples

Soil samples used in this study consisted of 33 soils collected from five German national parks from a wide range of climate conditions, parent materials, and vegetation types. Soils under native vegetation and extensive land uses (i.e., pastures and meadows) were sampled as relatively under-disturbed examples to consider soil features and regulation processes not concealed by different soil managements. Soil samples were collected in summer 2008 up to a 30-cm depth by horizons, air-dried, and sieved to <2 mm. The sampling depth was chosen to be comparable the with plow horizon of agriculture soils.

Total organic carbon (C_{org}), nitrogen (N) and sulfur (S) contents were determined by combustion with an elemental analyzer (Elemetar Vario EL III). The content of carbonates was detected by repeated elemental analysis before and after treatment of soils with HCl. Particle size distribution was performed according to DIN/ISO 11277 (2002) to determine sand, silt, and clay contents. The field water retention capacity was determined on ceramic plates at pF 1.8 according to DIN/ISO 11274 (2001). A brief description of the site locations and soil samples is given in Table 1.

Incubation experiments

Basal respiration experiments were carried out using the RESPICOND device from Nordgren Innovations (Sweden). Twenty grams of soil was placed in a vessel with a small container of 10 mL of 0.6 M KOH solution suspended above. Electrical conductivity of the solution was measured to monitor the CO_2 evolution during varying time intervals. Initially, values were recorded every 30 min and at the end of experiments every 12 h. The KOH solutions were periodically changed to prevent saturation during the experiment. To establish optimal conditions for microorganisms in the incubation experiments, the air-dried soil samples were re-moistened with water to 76% of their field water retention capacity (pF 1.8) immediately before starting the experiments. The soil respiration measurements were carried out in four replicates, which are presented in this study as averaged values. Measurement of evolved CO_2 began immediately within 2 h after re-moistening and ended after 80 days at a constant temperature 20 °C.

Thermogravimetric analysis (TG)

The TG was carried out using Mettler Toledo TGA/SDTA 851 device. Air-dried soils samples of around 1 g were placed in 0.8-mL ceramic pans and heated from 25 °C up to 950 °C at a rate of 5 °C per minute. TG data were collected every 4 s. During analyses, the furnace and the sample were purged with the constant air stream of 76% relative humidity at 25 °C and flow rate of 200 ml min^{-1}.

To ensure comparable analyzing conditions, the preparation of air-dried and sieved soil samples for TG analyses included an additional sample conditioning for at least 2 weeks under 76% relative air humidity maintained with saturated NaCl solution.

Both incubated and non-incubated soil samples were analyzed by TG. Before the TG, the incubated soils were air dried again and conditioned at 76% relative air humidity to insure comparable experimental conditions.

Statistical analysis

In order to describe the relationships between both TG and incubation experiments, correlation analyses using least square linear regression were performed with the help of Microsoft Excel®. Presented significant data have a

Table 1 Basic characteristics of studied soils

Location	Land use	Coordinates	Altitude/m	# Sites	# Samples	pF 1.8/g kg^{-1}	Organic C/g kg^{-1}	N/g kg^{-1}	S/g kg^{-1}	Sand/%	Silt/%	Clay/%
Berchtesgaden	Pastures, forests/all types	N 47° 33′ E 12° 48′	1050–1330	6	12	260–890	11.3–272.5	0.13–1.39	0.02–0.18	15–52	38–51	0–34
Bayerischer Wald	Coniferous forests	N 49° 05′ E 13° 15′	740–1200	3	6	260–520	50.1–214.0	0.22–1.19	0.04–0.13	49–56	32–37	0–15
Hainich	Deciduous forests, marsh/moss	N 51° 04′ E 10° 25′	350–480	3	4	360–460	18.6–90.8	0.17–0.43	0.03–0.06	2–7	55–71	27–43
Harz	Mixed forests, meadows	N 51° 48′ E 10° 38′	430–1230	4	6	230–740	39.1–262.1	0.17–1.37	0.03–0.17	21–74	20–54	0–24
Schorfheide-Chorin	Mixed forests, meadows	N 52° 53′ E 13° 55′	90–120	5	6	110–720	8.4–165.0	0.05–0.95	0.01–0.26	63–90	6–27	0–10

coefficient of determination significant level of at least 95% probability ($R^2 > 0.6$), while coefficients with lower probability were not presented (white areas in respective figures).

The aim of the statistical evaluations in this study was the determination of the most relevant time periods during incubation and the most relevant temperature intervals in thermal analyses. The data obtained are aimed to serve as a background for detection of relevant components by new methodological design and research approaches.

Results and discussion

Chemical, biological, and thermal characteristics of soil samples

The soil samples collected from virgin sites and extensive land use showed a wide range of physical and chemical characteristics (Table 1) because of the different environmental conditions of sites in national parks and protected areas. Clay contents ranged from nearly zero to 41%, water contents at pF 1.8 from 110 to 740 g kg^{-1}, OC contents from 8.4 to 272 g kg^{-1}, etc.

Figure 1a shows the mean values of cumulative evolved CO_2 from all the 33 soil samples incubated under constant optimal moisture conditions (80% of pF 1.8) and constant temperature (20 °C). The highest respiration rate was at the beginning of respiration experiments immediately after the rewetting of the air-dried samples. With increasing incubation time, the respiration rates of all the samples slowly decreased.

An averaged TG profile of all the non-incubated samples and its derivatives (DTG) are reported in Fig. 1b. The DTG curve reveals the presence of two main stages occurring during the thermo-oxidative decay in the soil samples in accordance with previously reported data [5, 7, 11–14]. The mass losses in the first stage between room temperature and 150 °C are usually attributed to the moisture evaporation, whereas higher temperatures were ascribed mainly to the degradation of soil organic and inorganic matter. As can be seen in Fig. 1b, both stages cannot be clearly separated.

In previous studies, the mass loss from 105 to 550 °C was used for the determination of SOM content [14, 15]. As reported in Plante et al. [7] and references therein, the water elimination from various minerals and clays can hamper the accurate determination of SOM in this temperature range. In this case, the extraction of SOM or investigations of other individual soil components (e.g., clay minerals, water-soluble organic matter, etc.) cannot solve this problem. Mutual interactions and relationships among soil components, such as water, organic and

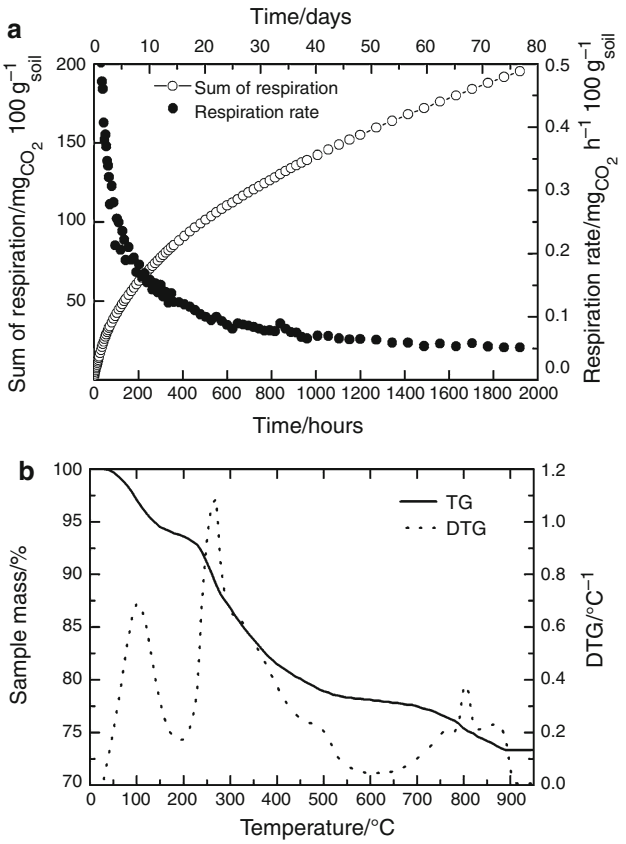

Fig. 1 **a** Soil incubation experiments, and **b** thermogravimetric analysis (TG) and its derivative (DTG)

inorganic matter, and soil biota, and their dynamic equilibrium represent intrinsic soil properties. Therefore, any extraction or chemical treatments ruin those interactions. In other words, it modifies (usually unknown) spatial arrangement of SOM, its chemical composition with unpredictable consequences for the physical, chemical, and microbiological behaviors of the whole soil. However, as it was demonstrated recently, that the problem of overlapping mass losses from different components can be reduced using narrow intervals of 10 °C temperature [5, 6].

Relationship between thermal mass losses and soil respiration

Siewert [5] found that TG detected mass losses of soils positively correlated with CO_2 evolution detected in incubation experiments. To verify these findings, the mass losses of investigated samples in 10 °C intervals were correlated with results of CO_2 evolution over the whole time of incubation. The coefficient of determination (R^2) was used as a measure of correlation closeness between results of both TG (temperature) and incubation (cumulative respired CO_2 and respiration rate).

Figure 2a and b reports the obtained linear determination coefficients calculated for mass losses and rate and cumulative CO_2 evolutions. In these figures, coefficients of determination are depicted in gray scale as the third dimension (*Z*-axis) to show how closely the results of both methods are related.

For the 33 investigated samples the significance of correlation coefficients starts at $R^2 = 0.6$, therefore the correlations below this limit are white (i.e., not shown). The gray scale is differentiated according to the significance of the correlation, i.e., the gray shade changes with 0.05 level increments up to 0.8 (of coefficient of determination) and then with 0.01 increments.

As seen in Fig. 2, the highest coefficient (R^2) is around 0.85 (the darkest areas correspond to the closest correlation) and can be found for interrelations between thermally induced mass losses during heating from 30 to 110 °C and the CO_2 evolution from soils under optimal wet conditions after 1 day of incubation (Fig. 2a). The second area with

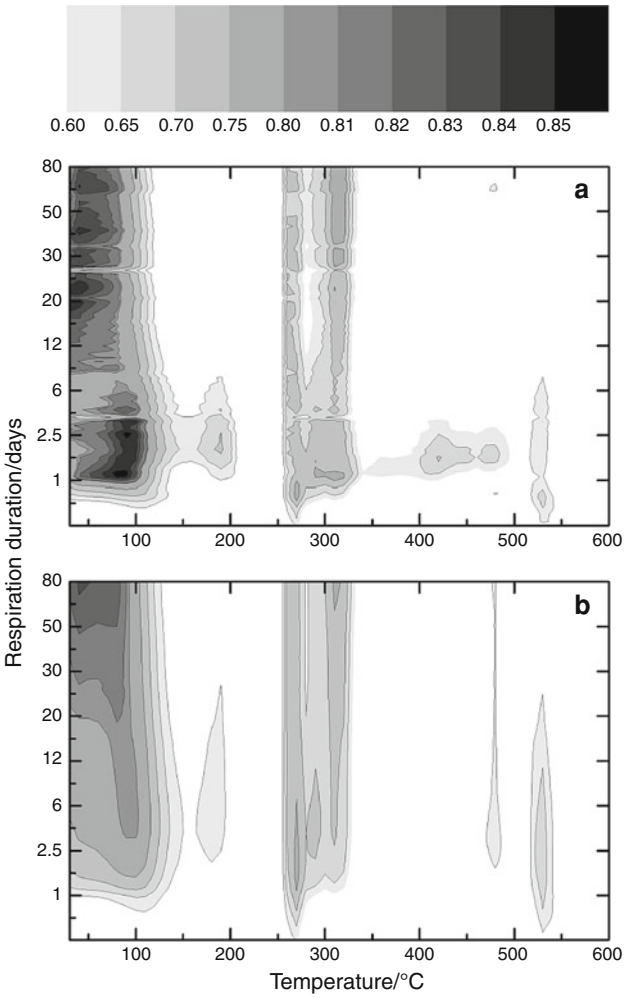

Fig. 2 Matrices of determination coefficients representing dependencies of evolved CO_2 from soil incubation experiment and TG mass losses. **a** Rate of CO_2 evolution and **b** cumulative evolved CO_2

statistical significance but with lower correlation coefficients is in the temperature interval from 260 to 320 °C and with respiration after approximately 1 day. Other significant correlations were also found between different incubation time periods and temperatures above 450 °C. Figure 2b demonstrates similar data but using the cumulative CO_2 evolution.

Since the thermally induced mass losses above 650 °C were very small and the correlation of these data to respiration was of low practical relevance, the presented data are reported only for temperatures up to 650 °C.

Normalization of thermogravimetric data to mass losses percent of carbon, clay, and nitrogen content did not increase the level of correlations. The same holds true for recalculation of the thermal mass losses in the temperature interval from 105 to 550 °C or using any other data combination. Similar effects were found for recalculated incubation data to percent of carbon content or clay content in the analyzed soil samples (not shown).

Considering this experience and the literature data, we conclude that the interactions between soil components, such as SOM, soil inorganic matter, and soil microorganisms, cannot be simply reduced to any single driving factor or any dominant component. Any recalculation should be done with an appropriate theoretical concept including possible influencing factors which have not been clarified yet.

Influence of incubation on the dynamics of thermal mass losses

In order to answer to which extend can TG reflect results of biological decay processes in soils, Fig. 3a shows the averaged mass losses of all samples before and after incubation experiments. To make the main changes more visible, the difference between both curves is reported separately in Fig. 3b.

Figure 3b illustrates an increase in thermal mass losses during respiration experiments at around 110 and 225 °C. This is in accordance with results of Plante et al. [16] who observed an increase in enthalpy of water vaporization in incubated samples using Differential scanning calorimetry (DSC). On the contrary, the incubated samples demonstrated reduced thermal mass losses at temperature above 240 °C, with a clear peak around 255 °C and smaller changes in the same direction above 280 °C. Again, in the experiments of Plante et al. [16], the reduced combustion enthalpy of non-incubated samples could be interpreted as a result of similar changes in soil composition as reported in this work.

Although the differences between averaged TG curves of incubated and non-incubated soil samples can be simply explained as microbial transformation and mineralization only, we can only speculate about the character of transformation processes taking into account available literature data.

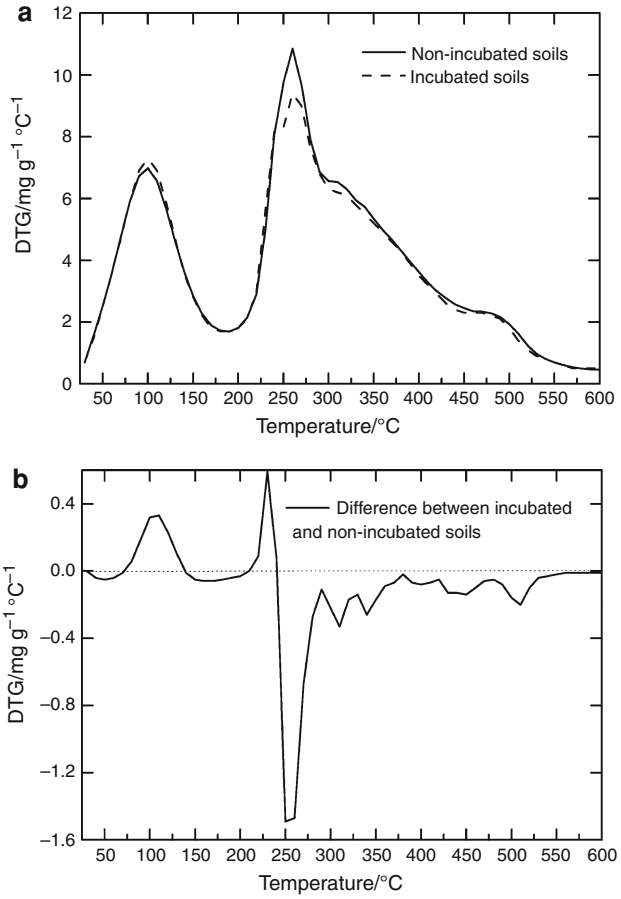

Fig. 3 Mean values of thermogravimetric data of incubated and non-incubated soils (**a**) and their difference (**b**)

If mass losses at around 110 °C are attributed to bound water, changes at this temperature caused by incubation experiments can be explained by (i) an accumulation of hygroscopic compounds such as polysaccharidic hydrogel-like exudates from microbiological activity [17] or accumulation of other exudates [18], (ii) the alteration and adaptation of SOM composition by growing microorganisms [5], (iii) redistribution of soil aggregates [19], (iv) chemical transformation of organo-mineral complexes [20], (v) pore size redistribution of SOM during wetting and swelling [21, 22], or (vi) combination of all the above or some others. The alternative "(i)" is slightly supported by an increase around 225 °C in which volatile or labile polysaccharides are probably eliminated, while the alternative "(vi)" is supported by a small shift of correlation coefficient to lower temperatures (increase in pore size) as depicted in Fig. 2a. A decrease at the higher temperature interval coincides with the mineralization and transformation of organic matter by microorganisms. Again, these results coincide with data obtained by DSC reported by Plante et al. [16].

Thermogravimetry (TG) or methods of thermal analysis have been for a long time recognized as methods useful for

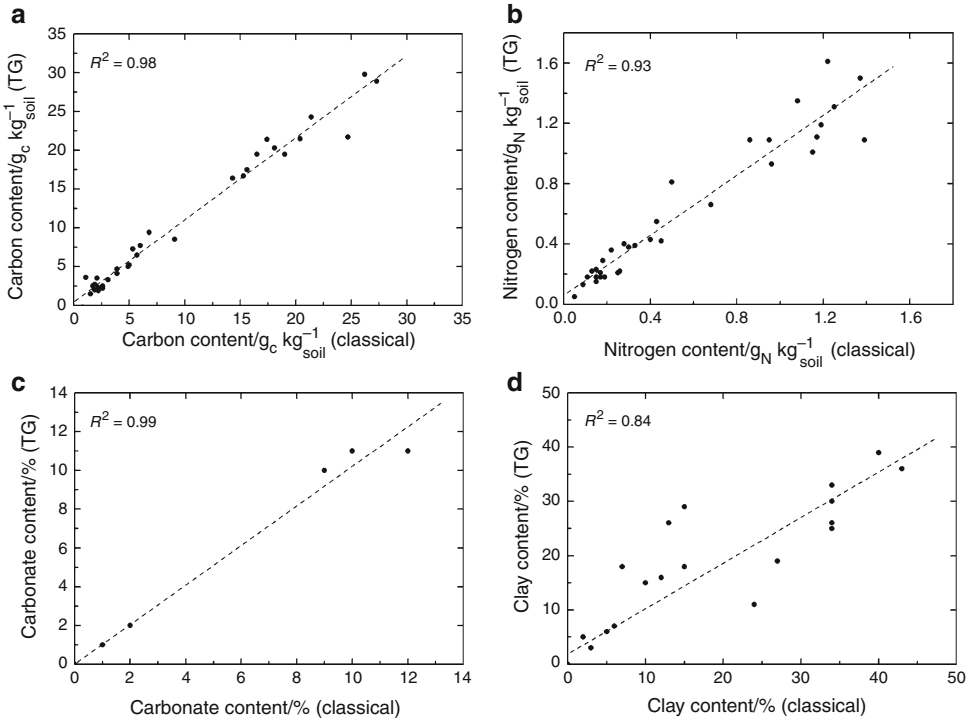

Fig. 4 Correlation between results obtained by TG (see equations) and organic carbon (**a**), organic nitrogen (**b**) contents determined by elemental (EA), and **c** clay content, **d** carbonate C determined by classical methods

prediction of stability of various materials (e.g., refs. [23, 24]). It can be concluded that TG mass losses could detect also changes in the soil composition in the course of soil mineralization and transformation and has the potential to predict soil respiration which must be validated with other sample sets. Nevertheless, the interpretation of processes will be possible as soon as the mechanisms of processes and composition of involved substances will be revealed.

Verification and extension of previous equations

The organic carbon content in soils is usually understood as a product of soil formation biological processes regulated by environmental factors. The possibility of SOC and nitrogen determination from TG mass losses was already demonstrated by Siewert [5, 6]. Since these possibilities do not exist in carbon-containing substrates with other origin than soil formation, one can speculate that the TG profiles somehow unravel biological processes regulating carbon and nitrogen content in soils. In order to verify these considerations, Fig. 4a–d shows a comparison of the total organic carbon, nitrogen, clay, and carbonate content obtained by TG and standard methods. For the determination of organic carbon content from thermal mass losses the following equation was used [5]:

$$\text{Carbon content} = (\text{thermal mass loss between 320 and 330°C} \times 1.18) - 0.05.$$

The result in Fig. 4a confirms the accurate determination of carbon content from thermal mass losses. Moreover, the equation seems to be applicable to a much greater range of soils than found before [6]. The same conclusion was found with respect to the nitrogen content (Fig. 4b). In this case, the total nitrogen content determined by elemental analyses correlates with thermal mass losses in temperature interval 260 to 440 °C using the equation:

$$\text{Total nitrogen content} = (0.00688 \times \text{mass loss}) - 0.02.$$

Figure 4c reports the comparison of carbonate content determined by elemental analysis and using the equation:

$$\text{Carbonate content} = (0.031 \times \text{mass loss between 540 and 950 °C}) - 0.34.$$

The clay content determined by pipette method was compared with clay content determined from TG by following equation:

$$\text{Clay content} = \text{mass loss between 520 and 530 °C}.$$

The results are reported in Fig. 4d.

In all cases, the quick and precise determinations of selected soil characteristics were confirmed.

Conclusions

The results confirmed an interrelationship between soil (rewetted to optimal water content) biological respiration estimated via CO_2 evolution and TG mass losses detected

in air-dried soils. These results confirm our working hypotheses but induced several questions which are connected mainly with correlations above 100 °C. Notwithstanding the explanation of these findings, results confirm the importance of standardized air drying of soil samples. Therefore, further research should discover the origin of bound water from clay, from fresh organic substances (e.g., bacterial polysaccharides), from humified substances or any other sources. The simplicity of TG experiments and the possible reflection of biological processes as an intrinsic property of soils make these future efforts attractive and a promising strategy.

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