

Application of thermogravimetric analysis for the evaluation of organic and inorganic carbon contents in agricultural soils

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Abstract The presented study focuses on the use of thermogravimetric analysis (TG) for estimating organic (OC) and inorganic carbon (IC) contents in bulk soils of different soil types and agricultural practices. Total carbon (TC) was measured by dry combustion using a total organic carbon (TOC) analyzer. The OC content was obtained as the difference between the TC and IC measurements. Regression equations were developed for relations between the thermal mass losses over various temperature intervals (200–370, 105–550, 110–420, 180–450, 250–440, 250–650, and 200–575 °C) and the OC content to determine the optimal temperature interval for the estimation of OC. The results for IC contents were related to the thermal mass losses at temperatures ranging from 500 to 800 °C. The results demonstrated that the thermal mass losses between 180 and 450 °C were fairly well related to the OC content ($R^2 = 0.63$), whereas the root-mean-square error of cross-validation (RMSECV) was too high (0.70 % OC). The inclusion of the clay content in the multivariate predictive equation did not importantly lower the RMSECV. By contrast, the thermal mass losses within the interval from 500 to 800 °C were closely related to the IC content determined using the TOC analyzer ($R^2 = 0.96$), with an acceptable RMSECV of 0.26 %. These results indicate that TG can provide a reliable estimation of the IC content but only rough estimations of the OC content in bulk soils of different types, bedrocks, and land uses.

Keywords Organic carbon · Thermogravimetry · Dry combustion · Inorganic carbon

Introduction

The soil carbon pool is composed of soil organic carbon (SOC) and soil inorganic carbon (SIC). SOC is a measure of the total amount of organic compounds or carbon within a soil, independent of the soil's origin or composition. SOC is of interest to soil scientists and researchers in related fields because of its importance to the principal physical, chemical, biological, and ecological functions of soil. SOC content is also a universal indicator of soil quality [1, 2]. Consequently, variations in the level of SOC can have serious implications for many environmental processes like soil fertility, erosion, and greenhouse gas fluxes [3]. The decline in SOC levels is recognized as a serious environmental threat [4]; however, the negative impacts of carbon sequestration on the ecosystem's health have long been neglected [5].

SIC includes lithogenic IC which is derived from parent material and pedogenic IC which is formed through the dissolution and precipitation of carbonate parent material. SIC can lead to carbon sequestration [6]. Although it can dissolve (particularly under acidic conditions), it is far less prone to loss than SOC [7].

Various methods are available for determining the SOC, and the choice of assessment method critically affects the SOC estimation. The two basic approaches to quantifying the SOC are wet and dry combustion. The Walkley–Black dichromate oxidation method [8] was used as a standard method in most soil-testing laboratories throughout most of the twentieth century [9]. This method is limited by a variable recovery percentage reported to be from 59 to

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88 %; however, this method is still used to measure SOC content because it is relatively rapid, simple, and inexpensive [10]. SOC is oxidized with potassium dichromate in the presence of concentrated sulfuric acid. The major drawback of this approach is the incomplete oxidation of the SOC, and thus a correction factor is required to adjust the SOC recovery. The quantities of SOC recovered vary with soil type, land usage, and even soil depth [11]. Since the method involves the use of concentrated sulfuric acid and Cr^{6+} , which is the toxic form of Cr, it is problematic with respect to both the working environment and general environmental concerns.

Loss-on-ignition (LOI) is a rapid, relatively inexpensive approach and is the most widely used method of directly estimating soil organic matter (SOM). In this method, a dried sample is heated to its ashing temperature, and the mass loss is assumed to be organic matter. The temperature of ignition must be high enough to completely remove organic matter and minimize mass losses due to dehydroxylation of clay minerals and breakdown of carbonates [9, 12]. The LOI combustion temperatures given in the literature vary between 375 and 800 °C [13].

At present, it is becoming increasingly common to apply dry combustion using automated instruments like total organic carbon (TOC) analyzers; elemental carbon, hydrogen, and nitrogen (CHN) analyzers; and gas chromatographs [10, 14]. The soil carbon is oxidized at high temperatures, followed by detection of the evolved CO_2 . Complete carbon oxidation is achieved, and thus, this method is considered to be most reliable for acidic soils, in which the OC content corresponds to the total carbon [15]. When soils which contain IC are analyzed, the IC should be removed prior to combustion or a separate determination of IC must be performed. Automated dry combustion is used in many studies as a reference for calibrating the results of other methods, because of its accuracy and reliability [12].

Thermal analysis has a long history in the geosciences. Most reports regarding the thermal analyses of soils have focused on the characterization of the mineral component, whereas organic components have received less attention [16, 17]. In a previous study, the SOM within three agricultural soil samples acquired in Serbia was determined from the mass loss within the interval 250–650 °C on the thermogravimetric analysis (TG) curve and compared with the results obtained using the Kotzman and Tyurin methods [18]. Miyazawa et al. [19] evaluated a thermogravimetric method for the determination of SOM within several Brazilian soils based on mass losses within the interval 110–420 °C and compared it with the Walkley–Black method, reporting a high correlation between the results of the two methods and certain distinct advantages of the TG method. Salgado et al. [20] calculated SOM in soils

acquired from Spanish forests affected by wildfires from the enthalpy of combustion obtained by differential scanning calorimetry (DSC) and by TG using the interval 200–575 °C. Linear correlations were found between the enthalpy of combustion of SOM measured by DSC and the organic matter content measured by TG. Siewert [21] correlated mass losses in Russian and German soils for each 10 °C temperature step from 30 to 1000 °C. A very good regression fit ($R^2 = 0.98$) between the SOC contents determined via dry combustion and the mass loss within the temperature interval from 340 to 350 °C was reported.

More recently, Plante et al. [16] published a review of the application of thermal analysis techniques in soil science, reporting two main exothermic DSC peaks attributed to the loss of organic matter in soils: The first one, at approximately 300–350 °C, was ascribed to the burning of carbohydrates and other aliphatic compounds, whereas a peak at 400–450 °C was ascribed to the loss of aromatic compounds. The effects of several experimental conditions have been studied for ensuring that reproducible and comparable results can be achieved when SOM quality is characterized using thermal techniques [17]. The possibility of using thermal analysis for characterization of SOM and interpretation of potential interferences from soil mineral matrix has been expanded by the application of an infrared analyzer based on $\text{CO}_2/\text{H}_2\text{O}$ evolved gas analysis [22]. Duguay et al. [23] studied SOM contents in abandoned agricultural fields after wildfires from mass losses between 105 and 550 °C after demineralization with HF and also reported two peaks—one at approximately 300 °C and another at approximately 440 °C. Thermal analysis has also been reported to be a useful tool for studying the composting process [24, 25], characterizing humic acids in forest soils [26], investigating changes in the quality of clay-associated organic matter in terms of thermal properties [27], studying organic matter conversion in cattle manure [28], and studying the behavior of sewage sludge and biochar from sewage sludge pyrolysis after addition to agricultural soils [29]. Correlations between soil respiration and its thermal stability determined by TG analysis were recently studied and published by Siewert and Kučerík et al. [30–32]. Recently, it has also been reported that TG has a promising potential for distinguishing organic carbon of pedogenetic origin from carbon of other sources [33].

In several studies that have focused on the characterization of SOM in bulk soils, isolated soil fractions, and composts, various temperature ranges have been adopted and ascribed to the loss of organic matter. Most of the published studies have focused on SOM quantification based on one single soil type (e.g., forest soils, soils affected by wildfires, or agricultural soils from one location). Thermal mass losses have been correlated with the OC contents obtained by different wet oxidation methods

which are not considered nowadays as a reference method for accurate determination of SOC. Although very good correlations have been reported, the uncommon use of TG for SOC determination, as well as different temperature ranges reported in the literature, suggests that some difficulties exist. Therefore, the objective of the presented work was to evaluate the capability of TG for simultaneous estimations of OC and IC in soils from various regions of Slovenia representing different land uses, bedrocks, and soil types. Regression equations were calculated between the OC determined via the combustion method using a TOC analyzer and the thermal mass loss, and the effects of different temperature ranges and clay contents were examined.

Experimental

Soil samples

A total of 46 samples were collected from soil depths of up to 30 cm at 28 locations throughout northeastern Slovenia with different soil types [34], bedrocks, and land uses (Table 1). Soil heterogeneity according to organic and inorganic carbon contents was the main reason for selecting those locations which are derived from different bedrocks, soil types, and land uses. The clay fraction was determined using the pipette method [35].

Chemical analyses

The samples were air-dried, ball-milled for 8 min for homogenization, and analyzed for OC. The measurements of OC and IC were taken using a TOC analyzer with a SSM-5000A solid sample module (Shimadzu 5050A with SSM-5000A, Shimadzu, Kyoto, Japan). For the TC determination, sample quantities between 0.500 and 1.000 g were weighed into the sample boat and combusted at 900 °C in the presence of an oxidation catalyst. The evolved CO₂ was carried to a non-dispersive infrared (NDIR) gas analyzer. The IC was measured at 200 °C after acidification of the sample with H₃PO₄ (85 %). The measurements were taken in accordance with ISO 10694 [36]. The OC content was obtained as the difference between the TC and IC measurements. Measurements were taken in triplicate for each sample.

Thermal analysis

The soil samples were air-dried and ball-milled as described for the carbon analysis. TG was performed using a METTLER TA 4000 system within the temperature range

30–800 °C in dynamic air with a flow rate of 100 mL min⁻¹ and a heating rate of 10 °C min⁻¹, using Al₂O₃ crucibles and sample masses of approximately 10 mg. The measurements were repeated at least three times for each sample. We evaluated the mass losses of bulk soils over various temperature ranges cited in published papers: 105–550 °C [23], 110–420 °C [19], 180–450 °C [17], 250–440 °C [21], 250–650 °C [18], and 200–575 °C [20]. For selected samples, additional TG measurements were taken after pretreatment with HCl in order to remove IC [23].

Statistical analysis

The organic and inorganic carbon contents obtained using the TOC analyzer (considered as a reference method) were used to develop regression equations using the predictor variables of thermal mass loss for different temperature intervals and clay contents, which varied between 4 and 42 % (Table 1). The dataset consisted of 46 samples for which averages of three analytical replicates of OC, IC, and thermal mass losses within various temperature intervals were used. Predictive models for the response variables OC and IC were fitted using the linear regression method. Univariate and multivariate models were developed. As a prediction variable, in the univariate cases, thermal mass losses of untreated soil samples over various temperature intervals were used, and in multivariate cases, the clay content was added as a predictor. Part of the analysis for response variable OC was carried out on 43 samples, because three samples were detected as outliers (Fig. 3). In the regression analysis with response variable IC and prediction variable thermal mass loss in the temperature interval 500–800 °C, 29 samples with inorganic carbon content more than 0.1 % were included. Part of the analysis for response variable IC was carried out on 26 samples because three samples were detected as outliers (Fig. 4). The goodness of fit was assessed using the R^2 parameter, and the model performance was evaluated in terms of the root-mean-square error of leave-one-out cross-validation (RMSECV) [37]. The analyses were performed in R Core Team [38] using the DAAG library [39] for cross-validation.

Results and discussion

The mean values of three independent measurements for the SOC contents for all the studied areas obtained using the elemental analyzer were between 0.38 and 26.1 %, whereas the SIC contents were between <0.1 and 7.07 % (Table 1).

Table 1 List of soil samples according to location, land use, bedrock, and soil type

Location	Name	Clay/%	SOC/%	SIC/%	Land use	Bedrock	Soil type [34]
Gačnik	1	39	1.79	2.27	Orchard	Marlstone	Eutric Cambisol
	2	36	1.52	2.51			
	3	40	0.91	2.96			
Gačnik	4	40	1.23	2.97	Orchard	Marlstone	Eutric Cambisol
	5	35	0.76	2.99			
	6	42	0.38	3.04			
Pivola	7	10	2.50	<0.1	Orchard	Metamorphic rocks	Dystric Cambisol
	8	17	1.91	<0.1			
	9	22	1.60	<0.1			
Zrkovci	10	5	5.04	1.46	Pasture	Alluvial deposits	Dystric Fluvisol
	11	6	2.75	1.71			
	12	4	1.35	1.98			
Slov.	13	10	2.94	5.13	Pasture	Alluvial deposits	Eutric Fluvisol
Konjice	14	9	1.54	6.58			
	15	11	1.20	7.07			
Konjiška Gora 1	16	33	4.34	<0.1	Forest	Sedimentary carbonate rocks (limestone)	Rendzinic Leptosol
	17	31	1.93	<0.1			
	18	23	1.14	<0.1			
Konjiška Gora 2	19	23	2.87	4.16	Forest	Sedimentary carbonate rocks (dolomite)	Rendzinic Leptosol
	20	25	1.41	4.08			
	21	29	0.54	3.16			
Škalce	22	14	2.83	1.13	Vineyard	Colluvium	Eutric Cambisol
	23	20	1.66	0.29			
	24	17	0.79	<0.1			
Kozjak	25	18	3.84	0.22	Cropland	Metamorphic rocks	Dystric Cambisol
Galicija	26	28	2.22	<0.1	Pasture	Igneous rocks	Dystric Cambisol
Kupčni Vrh	27	25	2.40	1.75	Vineyard	Sandstone	Eutric Cambisol
Ptuj	28	16	2.97	0.54	Garden	Alluvial deposits	Eutric Fluvisol
Ptujška Gora	29	24	4.46	<0.1	Cropland	Pliocene deposits	Dystric Cambisol
Vurberg	30	18	2.33	0.12	Garden	Pliocene deposits	Dystric Cambisol
Markovci	31	21	1.58	<0.1	Cropland	Alluvial deposits	Dystric Cambisol
Oplotnica	32	16	3.41	0.47	Garden	Pleistocene deposits	Dystric Planosol
Slov. Bistrica	33	23	2.05	<0.1	Cropland	Pleistocene deposits	Eutric Planosol
Makole	34	12	1.11	0.35	Vineyard	Marlstone	Eutric Cambisol
Ptuj	35	17	1.02	<0.1	Cropland	Pleistocene deposits	Dystric Cambisol
Haloze	36	20	0.79	3.24	Vineyard	Marlstone	Aric Anthrosol
Bistrica ob Sotli	37	17	2.47	0.59	Orchard	Marlstone	Eutric Cambisol
Lovrenc na Poh.	38	16	2.90	<0.1	Pasture	Diluvium, colluvium	Dystric Cambisol
Pesnica	39	26	1.89	1.38	Cropland	Pleistocene deposits	Eutric Gleysol
Pernica	40	41	1.41	0.68	Pasture	Marlstone, sandstone	Eutric Planosol
Črna na Kor.	41	15	9.32	<0.1	Pasture	Metamorphic rocks	Dystric Cambisol
Stična	42	24	2.97	1.92	Vineyard	Sedimentary carbonate rocks (dolomite)	Chromic Cambisol
Bizeljsko	43	19	1.40	0.21	Vineyard	Marlstone	Eutric Cambisol
Pivola	44	14	26.1	<0.1	Forest	Metamorphic rocks	Dystric Cambisol
	45	16	12.3	<0.1			
	46	21	3.80	<0.1			

Thermal analysis

Figure 1 shows typical TG and derivative thermogravimetry (DTG) curves for three soil samples with different nature of soil organic matter and soil mineral matrix. Sample 3 represents an orchard soil with OC and IC contents of 0.91 and 2.96 %, sample 10 a pasture soil with OC and IC contents of 5.04 and 1.46 %, and sample 45 a forest soil with high OC (12.3 %) and very low IC contents (<0.1 %). The diagrams show the characteristic regions considered during the thermal analyses of the soil samples: In all samples, a mass loss within the temperature range up to 170 °C (DTG peaks between 50 and 55 °C) could be observed as a result of dehydration reactions. The decomposition of SOM occurred between 200 and 550 °C [16]. Two major stages were observed for samples with high OC (e.g., sample 45): The mass loss within the 200–320 °C range could be attributed to the combustion of carbohydrates and other aliphatic compounds, while in the second interval, 330–530 °C, thermal degradation of more stable aromatic structures occurred [17, 23, 26]. For samples with lower OC, only one broad step with a peak at 320 °C could be observed in this interval, whereas in soil samples with very low OC, the corresponding mass loss was barely visible. The mass loss above 600 °C could be attributed to carbonate thermal degradation, as reported in the literature [19, 26, 40]. The DTG curves for samples with higher IC displayed peaks at temperatures between 705 and 720 °C, whereas no comparable peaks were observed within this region for samples with very low IC.

Additional experiments performed using different heating rates (2, 5, and 20 °C min⁻¹) offered no important advantages in comparison with the results obtained by using a heating rate of 10 °C min⁻¹, which is in good agreement with published results. Although some studies have reported a slower heating rate of 5 °C min⁻¹ [18, 21], most researchers have used the heating rate of 10 °C min⁻¹,

which represents the best compromise between the time required for analysis and the peak resolution to determine soil organic matter [16, 17, 20, 23]. The selected temperature range was from room temperature to 800 °C. The upper temperature limit of 700 °C reported in some studies was too low for some of the samples analyzed in this study because the mass loss between 700 and 800 °C remained considerable, whereas at >800 °C, mass losses were negligible for all investigated samples.

Figure 2 presents the TG curves for pasture soil sample 13 (2.94 % OC and 5.13 % IC) before and after carbonate removal with HCl. The mass loss within the region between 180 and 450 °C, which was used to calculate the OC using the TG method, did not change after carbonate removal, whereas the mass loss between 500 and 800 °C changed from 24.8 to 1.9 %; thus, this finding offers additional proof that the mass loss within this range can be primarily attributed to the decomposition of inorganic carbonates being removed from the samples during HCl treatment.

Thermal mass loss: soil OC relations

Various temperature ranges have been reported for the oxidation of the organic components present in soils. These temperature differences can be ascribed to differences in organic matter composition; degree of humification [17, 27]; the interaction of organic components with the mineral surface, which may have a significant impact on the stabilities of those components [41]; land use, which can alter the quality of clay-associated organic matter [27]; and experimental conditions, which can influence the resulting curves [17].

The mass losses within the temperature intervals of 200–370, 250–650, 110–420, 200–575, 250–440, 105–550, and 180–450 °C were 1.0–3.4, 3.0–14.4, 1.4–5.3, 2.3–5.6, 1.1–4.6, 2.3–11.0, and 1.5–5.3 %, respectively. The mass

Fig. 1 Typical TG and DTG curves for three studied soil samples: (3) Gačnik, orchard; (10) Zrkovci, pasture; and (45) Pivola, forest

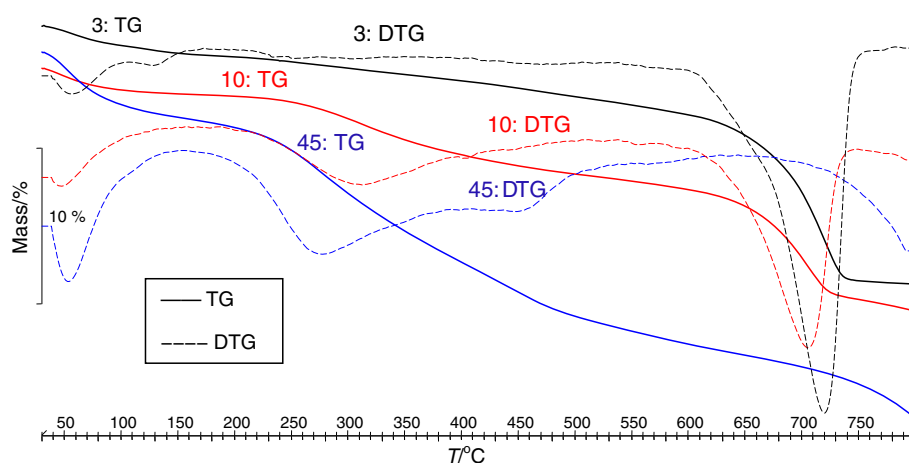


Fig. 2 TG curves for a typical soil sample with high inorganic carbon content of 5.1 % before and after carbonate removal with HCl

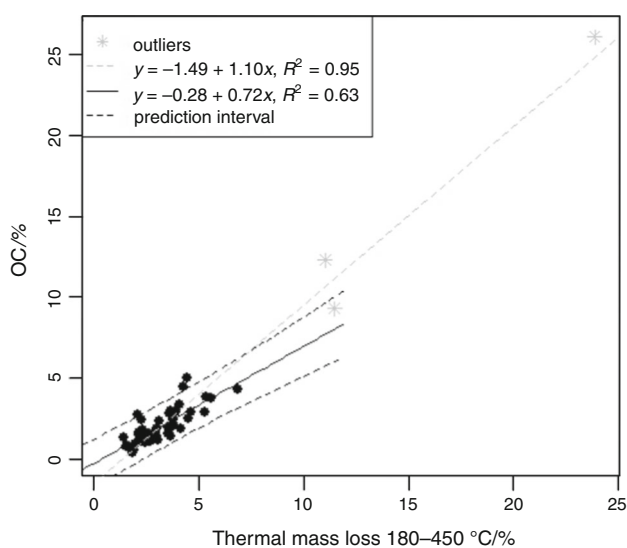
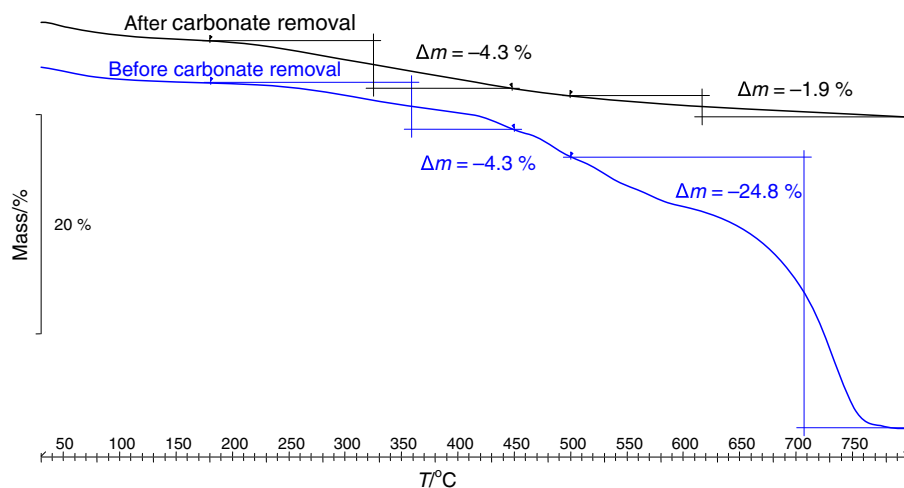


Fig. 3 Scatter plot of organic carbon (OC) versus thermal mass loss within the temperature interval 180–450 °C with corresponding regression lines fitted including or excluding outliers. Prediction intervals are shown for the regression line fitted excluding outliers

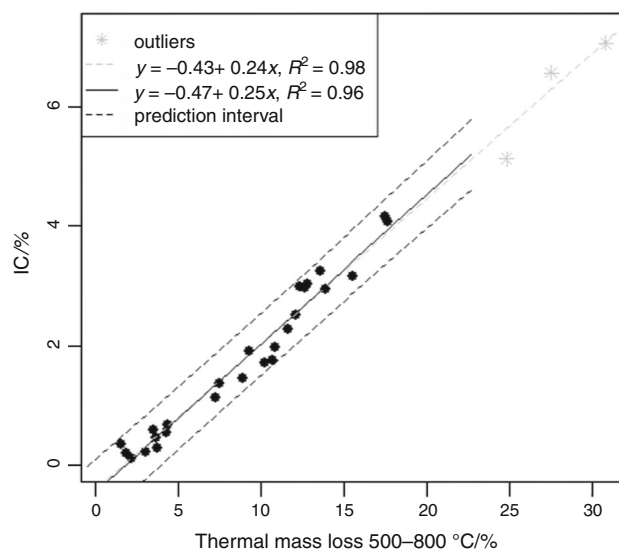


Fig. 4 Scatter plot of inorganic carbon (IC) versus thermal mass loss in the temperature interval 500–800 °C with corresponding regression lines fitted including or excluding outliers. Prediction intervals are shown for the regression line fitted excluding outliers

loss between 500 and 800 °C, which represents carbonate decomposition, ranged from 1.9 to 30.9 %.

The univariate regression analyses for response variables OC or IC and predictor variable the mass losses within temperature interval from 180 to 450 °C or from 500 to 800 °C, respectively, showed a good fit with R^2 values of 0.95 and 0.98. However, in regression models (Figs. 3, 4) with either of the two response variables (OC or IC), some samples with very high organic or inorganic carbon contents were detected as high leverage points (outliers) that highly influenced estimates and standard errors of linear regression coefficients and consecutively also R^2 values leading to unfair bias, especially in regression analysis with predictor OC. For that reason, they were excluded from the further analyses.

The relations between the OCs determined using the reference method and the mass loss values over different temperature intervals are described by the equations given in Table 2. The slopes (b) and intercepts (a) were found to be highly variable depending on the temperature interval, indicating the complicated nature of the decomposition processes. The intercept expresses the residual effects of factors other than organic compounds that contribute to the mass loss, e.g., hygroscopic and interlayer water loss, decomposition of carbonates, and dehydroxylation of clay minerals and metallic hydroxides [42, 43]. Within the region up to 200–250 °C, the thermal mass loss was mostly attributed to the loss of molecular water from salts and organic matter and to the dehydration of clay minerals,

Table 2 Coefficients, coefficients of determination (R^2), and root-mean-square errors of cross-validation (RMSECV) for linear regression models using the equation $OC/\% = a + b \cdot TG/\%$ for various temperature ranges

Temperature range/ $^{\circ}C$	a	b	R^2	RMSECV
200–370	−0.17	1.11 ^a	0.70	0.64
105–550	0.71	0.26 ^a	0.24	1.03
110–420	−0.27	0.72 ^a	0.60	0.73
180–450	−0.28	0.72 ^a	0.63	0.70
250–440	−0.17	0.85 ^a	0.63	0.70
250–650	1.37 ^a	0.12	0.08	1.15
200–575	1.07 ^a	0.20 ^a	0.17	1.10

^a Statistically significant at $\alpha = 0.05$

which lose most of their interlayer-bound water by 250 $^{\circ}C$ and a small remaining portion by 350 $^{\circ}C$ [18, 44], whereas carbonates begin to decompose above 500 $^{\circ}C$ [45].

The results suggest that the above-mentioned interfering effects inherent to the samples in temperature intervals with the upper limit lower up to 550 $^{\circ}C$ had no significant effect on the thermal mass losses, as none of the intercepts were significantly different from zero (p values were 0.508, 0.095, 0.401, 0.364, 0.571, respectively). However, these effects were particularly pronounced for intervals in which the upper temperature limit was >550 $^{\circ}C$. The intercepts of the regression curves developed for the mass losses within the temperature intervals 200–575 and 250–650 $^{\circ}C$ were significantly different from zero (Table 2), revealing that other reactions were associated with the mass losses. We assumed that the decomposition of carbonates was the major contribution to the mass losses above 500 $^{\circ}C$. Our assumption was supported by the results of multivariate regressions in which the clay content was included as a predictor in addition to the thermal mass losses which demonstrated that in our case, clay had no significant influence on the mass losses in temperature ranges with an upper limit above 440 $^{\circ}C$ (Table 3).

The predictive capabilities of the model for the temperature intervals 105–550, 250–650, and 200–575 $^{\circ}C$ were poor and not acceptable (Table 2) with average prediction errors (RMSECV) more than 1.0 % OC. For the other evaluated temperature intervals, the regression equation for estimating the OC from the thermal mass loss in the interval 200–370 $^{\circ}C$ exhibited the highest R^2 value, 0.70, and the lowest average prediction error (RMSECV), 0.64 %. The temperature range up to 320 $^{\circ}C$ is associated with the combustion of carbohydrates and other aliphatic compounds, whereas the thermal degradation of the more stable fraction occurs up to 530 $^{\circ}C$ [17, 23, 26]. The TG curves in Fig. 1 indicate that the degradations of those soil

Table 3 Coefficients, coefficients of determination (R^2), and root-mean-square errors of cross-validation (RMSECV) for linear regression models using equation $OC/\% = a + b \cdot TG/\% + c \cdot clay/\%$ for various temperature ranges

Temperature range/ $^{\circ}C$	a	b	c	R^2	RMSECV
200–370	0.41	1.08 ^a	−0.02 ^a	0.74	0.60
105–550	1.37 ^a	0.23 ^a	−0.02	0.28	1.04
110–420	0.43	0.71 ^a	−0.03 ^a	0.67	0.68
180–450	0.24	0.69 ^a	−0.02	0.66	0.69
250–440	0.26	0.81 ^a	−0.02	0.65	0.70
250–650	2.16 ^a	0.09	−0.03	0.15	1.15
200–575	1.74 ^a	0.17 ^a	−0.02	0.22	1.11

^a Statistically significant at $\alpha = 0.05$

samples which were included in the regression analyses were not complete at 370 $^{\circ}C$; the more stable organic compounds were oxidized up to 450 $^{\circ}C$ (Fig. 1). The temperature range 180–450 $^{\circ}C$ was selected for determining the thermal mass losses since it covered more of the range of organic compounds' decomposition. The relation between the OC content measured using the TOC analyzer and the thermal mass loss (TG) within the interval 180–450 $^{\circ}C$ is illustrated in Fig. 3. Each data point represents an average value from three replicate measurements. The R^2 value was slightly lower (0.63) than the R^2 obtained for the interval 200–370 $^{\circ}C$ (0.70). The inclusion of the clay content in addition to thermal mass losses in bivariate regressions was significant in the temperature intervals 110–420 and 200–370 $^{\circ}C$, but little improvement in the R^2 value was observed, whereas for all other studied intervals, the impact of the clay content was insignificant (Table 3). Some reasons for the weak relationship may be the fairly narrow range of SOC (0.38–5.04 %), the highly variable ratios between clay and SOC contents (1:1–110:1) indicating the different proportions between water fractions [46], sample compositions, and heterogeneities of soil organic compounds as soil samples derived from different soil types, bedrocks, land uses, and agricultural activity.

The relation between the mass loss within the temperature interval 500–800 $^{\circ}C$ and the IC content can be described using the following regression equation: $IC/\% = -0.47 + 0.25 \cdot TG/\%$. The results indicated a good fit ($R^2 = 0.96$) of the regression line between the mass loss and the IC content obtained using the elemental analyzer (Fig. 4) and an RMSECV of 0.26 %. Nevertheless, the significant negative intercept may suggest that the mass loss in this temperature interval can be partially attributed to the decomposition of soil components other than carbonates. The inclusion of clay content as a predictor in the multivariate regression revealed that clay had no significant effect on the thermal mass loss in this interval, and thus, the

interfering effects were likely caused by the decomposition of organic carbon of high stability.

Conclusions

TG, which has been applied extensively in clay mineralogy, is problematic for the quantitative determination of the OC in bulk soil samples because the thermal mass losses are the result of various decomposition reactions in addition to the combustion of organic matter. Some of these interfering effects can be eliminated by choosing a temperature interval in which the lowest and highest temperatures are between 180 and 450 °C. Regression equations developed for intervals within this range possessed insignificant intercepts. In the temperature interval 180–450 °C, the regression model developed using the mass loss as the predictor and the OC determined using a TOC analyzer as the response variable exhibited a good fit; however, the RMSECV was too high (0.70 % OC) for reliable estimation of the OC in investigated soil samples. The inclusion of the clay content as a predictor in addition to the mass loss did not lower the RMSECV and, in our case, had a negligible effect. However, the thermal mass losses within the interval from 500 to 800 °C were closely correlated with the IC contents obtained using the TOC analyzer. The R^2 of 0.96 and the acceptable RMSECV of 0.26 % IC demonstrated that thermal analysis could provide reliable predictions of the IC content in soils containing at least 1 % IC. Thermogravimetry appears to be a suitable technique for the prediction of IC, but may be useful only when rough estimates of the OC in bulk soils of different soil types developed on different bedrocks, land uses, and agricultural activities are required.

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