

DIVISION S-5—PEDOLOGY

Rapid Screening of Soil Properties using Thermogravimetry

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ABSTRACT

Organic C, N, clay, and carbonate content are basic soil properties, which are commonly assessed by different analytical methods. This study aimed at utilizing temperature-induced dynamics of weight losses to determine these parameters simultaneously without losing precision and accuracy. For this purpose, thermogravimetric profiles of 52 soil samples were recorded and compared with C, N, and textural data obtained from conventional analyses using dry combustion and pipette methods. The samples originated from different climatic regions, land-use systems and parent materials. The results showed that thermal weight losses correlated closely ($P < 0.001$) with the content of organic C ($R^2 = 0.98$), total N ($R^2 = 0.94$), clay ($R^2 = 0.87$) and $\text{CO}_3\text{-C}$ ($R^2 = 0.99$) for mineral soil samples, while no such relationships were found in organic soil horizons. For mineral soils, each soil property correlated with a specific interval of temperature-induced weight losses. Application of thermogravimetry to independent additional sets of 250 samples confirmed a reliable estimation of organic C, total N, clay and $\text{CO}_3\text{-C}$ of mineral soils. It is concluded that thermogravimetry allows a simultaneous, rapid and reliable screening of these four properties in mineral soils.

SOIL ORGANIC MATTER along with clay and carbonate content are key parameters that affect the global cycling of elements and the response of soils to global warming and land-use change. The reliable prediction of such parameters requires a huge database. Its establishment, however, is hampered by the need to use different analytical methods. To save costs and time, it would be helpful to have a method that allows the simultaneous screening of basic soil properties. The thermogravimetric method provides similar estimation of organic and mineral C, total N, and clay values to common analytical methods, but it has the advantage to combine in one method the four analyses with a very simple procedure and sample preparation.

Historically, soil organic matter concentrations were estimated from dry combustion, that is, from heating soil for 180 min at 550°C (Schlichting et al., 1995; Soil Survey Staff, 1996, Method 6A2a). This method may lead to false results in mineral soils, because clay minerals lose adsorbed and crystal lattice water upon heating (Dyal et al., 1941; Velayutham, 1972). In addition, carbonate may interfere with the analysis, due to partial decay of carbonates (Liptay, 1974). Yet, little attention has been paid to using the dependency of the thermally induced weight losses from clay and carbonate content

for simultaneously determining these parameters with the content of soil C and N. This, however, should be possible when considering that combustion of organic matter, loss of clay-associated water and decay of carbonates occur at different temperature intervals (Gaál et al., 1994; Kristensen, 1990; Liptay, 1974).

In thermogravimetry, the dynamics of weight loss can be continuously recorded over the whole temperature range from 25 to 1000°C. This allows identification of temperature areas with overlapping weight losses from different and individual components and development of mathematical evaluation algorithms of thermogravimetric curves for calculation of soil properties with maximum accuracy. On this basis, the objective of this study was to evaluate the use of thermogravimetry as a method for simultaneous screening of soil organic C, total N, $\text{CO}_3\text{-C}$, and clay content.

For this purpose, the study was performed with soils from climate sequences in Russian Lowlands and Germany and evaluated using different soil sample sets from the same and other geographic regions.

MATERIALS AND METHODS

For method development, 48 topsoil and 4 subsoil samples were selected from different geographic locations across the Western Russian lowlands and central Europe in Germany. Land uses comprised native vegetation, forest plantations and long-term agricultural field experiments. The samples covered a wide range of organic matter, clay, and carbonate contents. Soils were mainly Mollisols and Alfisols (Table 1).

Method evaluation was performed using independent series of samples: 105 soil samples originated from transects across the West Siberian plain from the Southern taiga to the steppe, and across the Altai mountains from the mountain tundra to the desert near the Mongolian border. In addition 54 samples from 12 long-term agricultural field experiments in Germany, 28 samples from Antarctica, 14 samples from tropical forests and agricultural soils in Costa Rica, and 33 Vertisols from Gezira Region in Sudan under agricultural use and permanent fallow were tested. Details concerning soil types and properties are given in Table 2.

All samples were air-dried, and sieved to <2 mm before analysis. Soil pH was determined in 0.01 M CaCl_2 in a 1:2 suspension (Soil Survey Staff, 1996, Method 8C1e); the cation exchange capacity (CEC) was analyzed as sum of ammonium acetate extractable bases (Soil Survey Staff, 1996, Method 5A3a); particle-size determinations were made on the <2-mm sample (Soil Survey Staff, 1996, Method 3A1) by removing organic matter with H_2O_2 , wet sieving to remove the sand and coarse silt; the clay and fine silt were separated by pipette. The determination of water retention was performed with pressure-plate extraction after rewetting air-dried samples at a pressure of 6 kPa (pF 1.8) (Soil Survey staff, 1996, Method 4B1e). Total C and N were estimated on ground aliquots by

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Table 1. Samples used for method development.

| N† | Soil taxonomy | Soils ‡ | Localities | Land uses | Clay | g kg ⁻¹ | | |
|----|-------------------------------|-----------------------------------|---------------------------------|---|---------|--------------------|----------|----------------------|
| | | | | | | SOC§ | Total N | CaCO ₃ -C |
| 6 | Xerolls, Calcixerolls, Udolls | Calcic Chernozems | Rostov, Russia | unused natural dry steppe, agricultural fields, forest plantations | 90–420 | 11–27 | 0.8–2.5 | 0–0.1 |
| 7 | Udolls, Ustolls | Haplic Chernozems and Phaeozems | Kursk Biosphere reserve, Russia | natural steppe and forests, agricultural fields; permanent fallow | 330–370 | 33–58 | 2.4–4.5 | 0–0.01 |
| 7 | Ustalfs | Podzoluvisols | Moscow, Russia | natural broad-leaf forests, agricultural fields, horticulture, forest plantations | 110–160 | 19–34 | 1.3–1.9 | 0 |
| 10 | Ustalfs, Udepts | Podzoluvisols | Zagorsk, Russia | native forests, agricultural fields, pasture lands, natural succession | 170–330 | 4–26 | 0.4–1.7 | 0–1.1 |
| 8 | Udolls, Ustepts, Ustalfs | Haplic Phaeozems; Podzoluvisols | Sachsen-Anhalt, Germany | agricultural fields, forest plantations | 110–550 | 6–30 | 0.5–2.6 | 0–3.8 |
| 3 | Udolls | Degraded Chernozems | Bad Lauchstädt, Germany | >100 yr cropping experiment with mineral and organic fertilizers | 210–230 | 22–29 | 0.20–2.7 | 0 |
| 6 | Inceptisols, Ustalfs, Udolls | Rendzina, Podzoluvisols, Gleyzems | Bayreuth, Germany | forest plantations, agricultural fields | 220–480 | 8–59 | 0.6–3.2 | 0–0.1 |
| 5 | Udolls, Ustalfs | Luvissols, Chernozems | Hildesheimer Börde, Germany | forest plantations, agricultural fields | 140–360 | 5–36 | 0.4–2.8 | 0–0.2 |

† Number of samples selected.

‡ FAO, ISSS, ISRIC (1998).

§ SOC is soil organic C.

dry combustion at 1060°C and detection of evolved CO₂ and N₂ using a Carlo Erba element Analyzer (Carlo Erba, Italy). Soil CO₃-C was released from soil after lime dissolution with HCl, trapped in KOH and quantified as CO₂-C by electric conductivity monitoring at a Respirocond system (Nordgren Innovations AB, Bygdeå, Sweden).

For thermogravimetric analysis, only sieved samples were used. Grinding the soils did not result in more reproducible

results (data not shown). To standardize air-drying, samples were equilibrated for at least 2 wk at 76% relative air humidity, which was maintained using saturated NaCl solution. To identify weight losses by water saturation of hygroscopic properties, the first 52 samples were additionally analyzed after equilibration at 100% relative air humidity and after drying across silica gel, reaching equilibrium water content of <25% relative air humidity.

Table 2. Samples used for method verification and evaluation.

| N† | Sampling time | U.S. soil taxonomy | Localities | Land uses | Clay | g kg ⁻¹ | | |
|-----|---------------|--|--|---|---------|--------------------|---------|----------------------|
| | | | | | | SOC‡ | Total N | CaCO ₃ -C |
| 105 | 1998 | Mollisols, Alfisols, Spodosols, Inceptisols, Gelisols, Ultisols | Transect across Western Siberia from Plotnikovo via Tomsk, Kotorovo, Barnaul, Cherga, to Seminsk pass | native dry steppe, natural forests, agricultural fields, forest plantations | 20–520 | 2–110 | 0.2–5.5 | 0–31.7 |
| 160 | 2000 | Mollisols, Alfisols, Spodosols, Inceptisols, Gelisols, Ultisols, Histosols | Transect across Western Siberia from Plotnikovo via Tomsk, Kotorovo, Barnaul, Cherga, Seminsk pass, Aktasch to Beltir | native dry steppe, natural forests, agricultural fields, forest plantations, semi-desert and desert | 40–690 | 2–31 | 0.2–2.5 | 0.4–42 |
| 54 | 1999–2001 | Mollisols, Alfisols, Spodosols, Inceptisols | Seehausen, Salzungen, Spröda, Methau, Bad Lauchstädt, Müncheberg, Lauterbach, Groß Kreuz, Prag, Thyrow, Pouch, Germany | agricultural field experiments, plots with different organic and mineral fertilization | 110–230 | 3–27 | 0.3–2.4 | 0 |
| 28 | 1996 | Gelisols | King George Island, Antarctica | virgin lowlands, mostly no vegetation cover | 130–400 | 7–32 | 0.5–25 | 0 |
| 14 | 1999 | Andosols, Oxisols, Alfisols | National parks in Monteverde, Rincón de la Vieja, Manuel-Antonio, Carara, Irazu, Costa Rica | natural forests, meadows, agricultural fields, fruit plantations | 140–550 | 15–105 | 1.8–6.2 | 0–0.6 |
| 33 | 2000 | Vertisols | Gezira Region, Sudan | agricultural fields, permanent fallow | 550–780 | 52–130 | 0.8–1.6 | 2.3–12 |

† Number of samples selected.

‡ SOC is soil organic C.

Thermogravimetric profiles were recorded on 0.5- to 1.2-g sample weight using a Mettler-Toledo SDTGA 851^e thermobalance (Mettler-Toledo GmbH, Zurich, Switzerland). Initial temperature was 25°C. A heating rate of 5°C min⁻¹ was used up to the final temperature of 950°C. During heating, every 4 s temperature-dependent weight loss was written down and the soil sample was spooled using an air current of 200 mL min⁻¹ with 76% relative humidity at 25°C.

RESULTS AND DISCUSSION

Thermogravimetry records the loss of soil components upon heating. Hence, soils with a different material composition produce weight loss signals of different intensity. For instance, the clayey sample exhibited higher weight losses at each temperature range than the sandy sample (Fig. 1), with the most intense signals occurring at around 100 and 300°C (Fig. 1a).

In contrast, the sample rich in carbonates revealed a

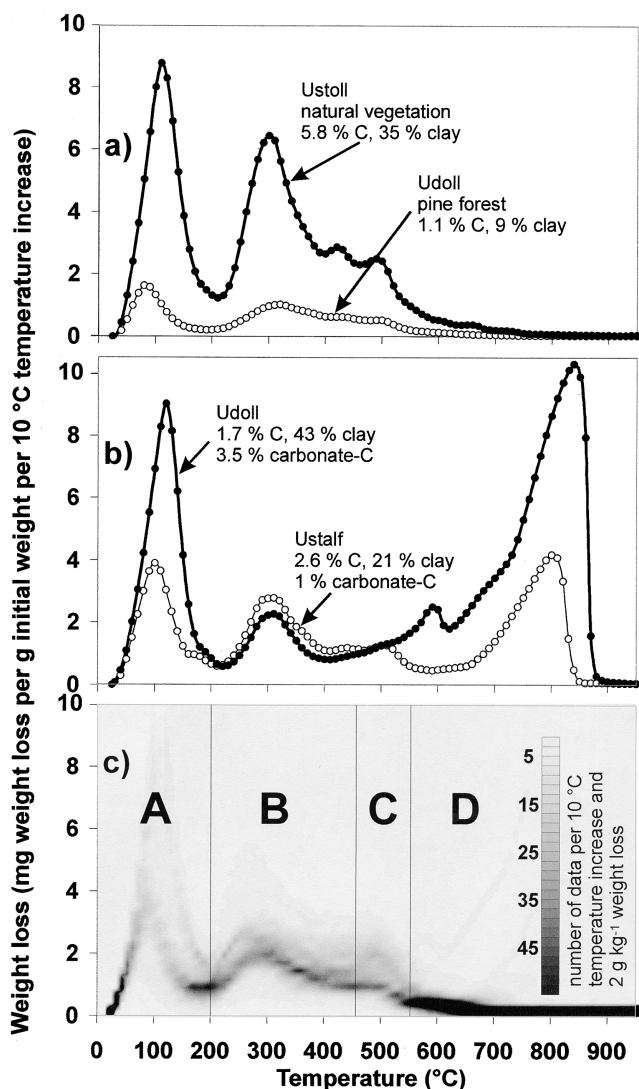


Fig. 1. Examples for thermogravimetric profiles of (a) soils with different clay and (b) different carbonate contents as well as (c) the absolute abundance distribution of all samples shown in Table 1. The capital letters indicate the characteristic temperature intervals for the removal of water (A), thermolabile (B) or stable (C) organic matter, and lime (D) during heating.

pronounced weight loss at temperatures exceeding 550°C (Fig. 1b). Repeating the measurement for a given sample reproduced both the shape of the curve and the difference between curves (data not shown). Hence, different soil properties are reflected in different thermogravimetric profiles (Kristensen, 1990; Golebiowska et al., 1996). The variations amongst these profiles allow the quantitative assessment of soil properties (Fig. 1c).

The density distribution of all 52 thermogravimetric profiles revealed that four temperature intervals describe the thermal decay process of soils (Fig. 1c): losses in the temperature range of 0 to 200°C (denoted as A in Fig. 1c) are attributed to the loss of water, such as crystalline lattice water, hygroscopic water of salts and organic matter (Liptay, 1974; Schnitzer et al., 1974; Gaál et al., 1994). Decay of organic matter produced two peaks each for thermolabile and stable organic constituents (denoted as B and C in Fig. 1c, respectively). Semi-quantitative comparisons of respective peak heights confirmed that the weight loss in the temperature interval B depended on management and microbial activity in agricultural soils (Chernikov, 1988; Anhehrn-Bettinazzi et al., 1988; Peschke et al., 1991; Sevcova and Sidorina, 1988), whereas the peak heights about 500°C depended on soil genesis and clay content (Chernikov, 1988; Leinweber et al., 1993). Kristensen (1990) proposed to calculate the ratio of the weight losses attributed to thermolabile and stable compounds as a parameter of soil organic matter quality, but failed to relate the thermogravimetric profiles quantitatively to soil properties. Release of carbonate as CO₂-C occurs at temperatures above 550°C (denoted as D in Fig. 1c; Liptay, 1974; Gaál et al., 1994).

Reliable measurement of mineral and organic C, total N content, and other soil properties from thermogravimetric profiles requires the use of all curve data. For this purpose, the weight losses for each 10°C temperature step from 30 to 1000°C was calculated and correlated with soil properties obtained from conventional analyses. This yielded in 97 individual regression functions for each soil property, most of them being nonsignificant at probability level of 95%. However, for certain 10°C intervals more than 98% of the variability of soil properties could be predicted by thermal weight losses. Figure 2 gives such an example for the correlation of

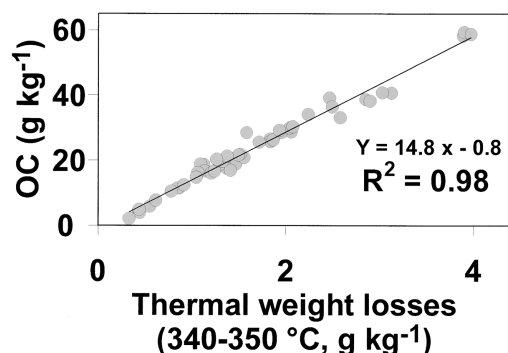


Fig. 2. Correlation between organic C (OC) with thermal weight loss from 340 to 350°C.

total organic C with the weight losses occurring between 340 and 350°C.

To illustrate which variation of weight losses in 10°C steps best explained the variations in soil properties, the coefficients of determination for every soil property were plotted versus temperature analysis (Fig. 3). Data points of the same soil property were connected using spline iteration. The results confirm that there are distinctly different temperature ranges at which a given soil property significantly correlates with thermogravimetric weight loss (Fig. 3). For instance, organic C and total N were described by weight losses between 250 and 450°C, whereas correlations with clay content yielded highest coefficients of determination at 120 and 530°C ($\geq 85\%$ explained variations). At a temperature above 600°C, mainly $\text{CO}_3\text{-C}$ affected the weight losses significantly, as has been presumed from the potential decay of carbonates. The same procedure was applied to larger temperature intervals (plots not shown). The use of smaller temperature intervals did not increase the level of coefficients of determination due to the influence of different soil thermal conductance and temperature distribution inside of the soil samples.

No significant relationships were found among weight losses and other soil properties such as water retention at pressure of 6 kPa (pF 1.8, maximum $r^2 = 0.35$), pH in 0.1 M CaCl_2 solution ($r^2 = 0.34$), cation exchange capacity ($r^2 = 0.19$), the ratio of organic C/N or sand and silt content ($r^2 < 0.2$ for all these three parameters). Rapid screening of soil properties other than organic matter, clay and lime content using thermogravimetry is hence either not possible or cannot be easily deduced from weight loss profiles.

The best 10°C-temperature intervals for the prediction of soil properties from weight losses were selected from Fig. 3. The regression functions used to predict organic C, total N, $\text{CO}_3\text{-C}$, and clay content were Number 1, 6, 11, and 14, respectively (Table 3). Applying

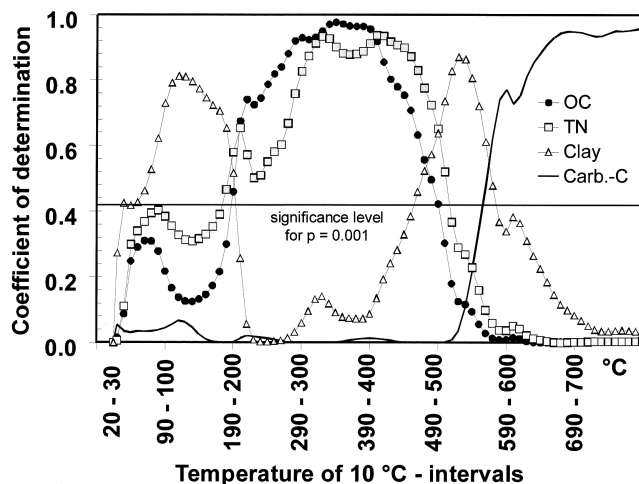


Fig. 3. Changes in explained data variability of different soil properties when correlated with the thermogravimetric data at different temperature intervals (OC: organic C, TN: total N, Carb.-C: $\text{CO}_3\text{-C}$).

these regressions to independent data sets obtained from soils outlined in Table 2 revealed that the accuracy of estimating organic C, total N, $\text{CO}_3\text{-C}$, and clay contents from thermogravimetric data was similar to those estimates obtained with separate standard methods of analysis (Fig. 4). It is concluded that thermogravimetry is a useful tool for rapid screening of mineral soils properties. However, few individual measurements still fell out of the 95% confidence interval calculated for the original Data Set 1. This finding demonstrates that the use of correlations as a tool for indirect screening of soil properties includes the risk that outliers will remain unseen. Hence, an additional quality control is required to ensure reliable data. This quality control consists of using additional temperature intervals for an independent estimation of soil properties from weight loss data. Table 3 summarizes the additional ten regression func-

Table 3. Temperature areas, regression parameters, theoretical accuracy, and calibration range for closest correlations between soil properties and thermal weight losses.

| Temperature area for weight losses | Regression equations† | Mean deviation | Calibration range | Coefficient of determination‡ | Equation number |
|------------------------------------|------------------------|----------------------------|-------------------|-------------------------------|-----------------|
| °C | | g kg ⁻¹ | | R^2 | |
| | | <u>Organic C content</u> | | | |
| 340–350 | OC = 1.48 WL – 0.08 | 2.1 | 4–58 | 0.977 | 1 |
| 250–440 | OC = 0.081 WL – 0.280 | 1.6 | 4–58 | 0.986 | 2 |
| 320–330 | OC = 1.18 WL – 0.05 | 7.0 | 2–110 | 0.914 | 3 |
| 110–550 | OC = 0.037 WL – 0.325 | 9.9 | 2–110 | 0.829 | 4 |
| 200–550 | OC = 0.058 WL – 0.601 | 7.2 | 2–110 | 0.907 | 5 |
| | | <u>Total N content</u> | | | |
| 400–410 | N = 0.1813 WL – 0.038 | 0.35 | 0.2–9.5 | 0.955 | 6 |
| 320–330 | N = 0.1118 WL – 0.023 | 0.38 | 0.2–9.5 | 0.950 | 7 |
| 300–500 | N = 0.00856 WL – 0.061 | 0.33 | 0.2–9.5 | 0.960 | 8 |
| 260–440 | N = 0.00688 WL – 0.020 | 0.31 | 0.2–9.5 | 0.967 | 9 |
| 300–380 | N = 0.0151 WL – 0.020 | 0.34 | 0.2–9.5 | 0.968 | 10 |
| | | <u>Carbonate C content</u> | | | |
| 810–820 | CC = 0.388 WL – 0.019 | 0.52 | 1–36 | 0.991 | 11 |
| 540–950 | CC = 0.031 WL – 0.34 | 1.27 | 0–38 | 0.949 | 12 |
| | | <u>Clay content</u> | | | |
| 110–120 | clay = 4 WL + 9.8 | 5.8 | 20–680 | 0.758 | 13 |
| 520–530 | clay = 27 WL + 1.0 | 3.9 | 90–560 | 0.870 | 14 |

† WL, weight losses in specified temperature area.

‡ All coefficients are significant at probability level of 99.9%.

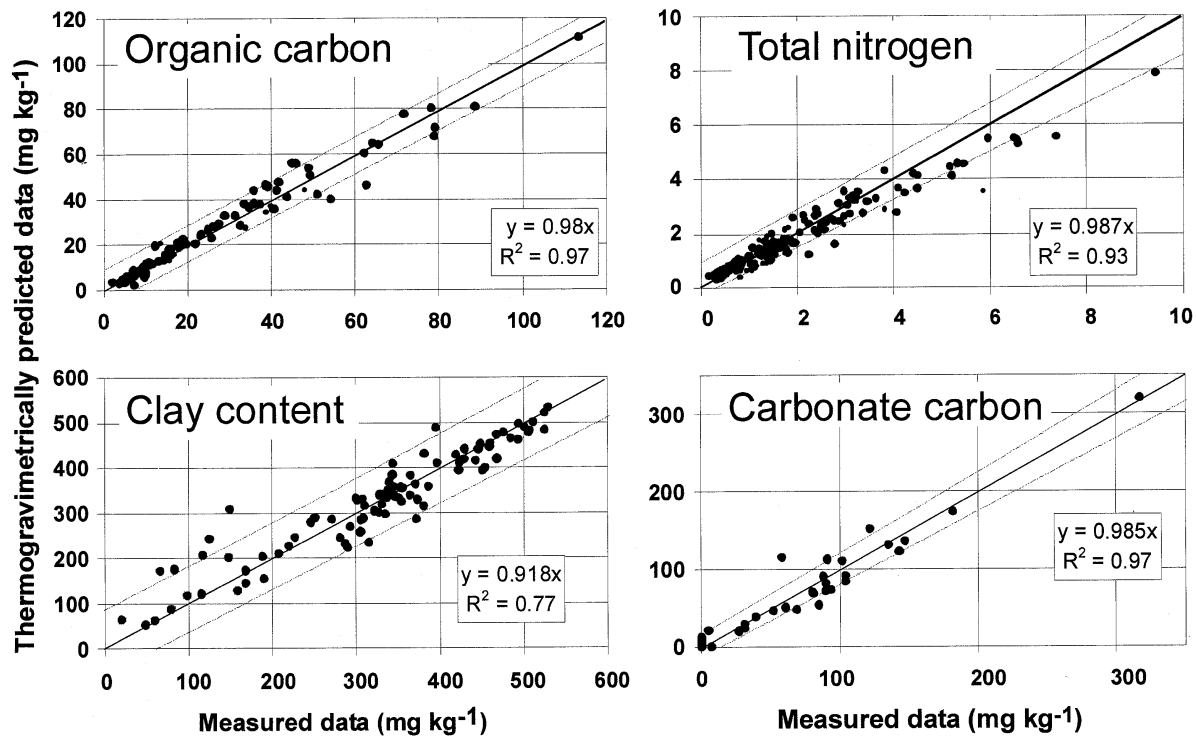


Fig. 4. Comparison of thermogravimetrically predicted soil properties (using the first fit in Fig. 3, original data set outlined in Table 1) with measured data (application of conventional analyses to the independent data sets for mineral soils of Table 2). The confidence intervals represent those of the original regression function of sample Set 1 (Table 1).

tions to be used for multiple estimation and quality control of thermogravimetric prediction of soil properties.

The multiple application of the linear regression functions revealed that within the range of soil properties tested no significant errors of determination for organic C, total N, CO₃-C, and clay content were observed (no one exception). However, in some instances this quality control implied that the criteria for reliability were not fulfilled despite the correct estimation of the mean of a given soil property. In these cases, the multiple application of regression functions hampered accurate predictions. This happened in up to 20% of samples containing charcoal, ashes, and other anthropogenic black C, and <4% of the samples from natural, forest, and agricultural soils.

In general, estimation of organic C, total N, CO₃-C, and clay content was possible within the range of soils tested. The quality control excluded soils from extreme conditions, that is, desert soils, soils heavily contaminated with anthropogenic substrates (e.g., with coals and tars), cryogenic tundra soils and soils with an aquatic moisture regime. Also organic substrates such as fresh plant materials, litter, composts or bog layers did not pass the quality control check (data not shown here). Such substrates might require other calibration tests not performed here. As a result, there was an upper limit for organic C content in mineral soils to be estimated with thermogravimetry. In the test samples this limit was 110 g C kg⁻¹.

CONCLUSIONS

Thermogravimetry provided to be a powerful indirect method for reliable estimation of organic C, total N, CO₃-C, and clay content of mineral soils. A quality control based on multiple parameter assessment provided a high level of certainty. The method is applicable to soil samples with a range of 2 to 110 g organic C kg⁻¹, 0 to 36 g carbonate C kg⁻¹, 0.2 to 9.5 N kg⁻¹, and 30 to 600 g clay kg⁻¹, but the quality control excludes desert soils and soils with an aquatic moisture regime, as well as organic rich or anthropogenic substrates. At the same time, these outliers render the method a potential diagnostic tool for identification of tar, coal, or other charred residues in soil. The multiple temperature dependence of weight loss from organic matter and clay content gives rise to the question which organic matter constituents and which organo-mineral associations control the shape of the thermogravimetric profile. In this context, elucidating these properties might extend the use of thermogravimetry to, for example, estimation of C subfractions of different decomposability and hence of different stable C pools in mineral soils.

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