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LOSS-ON-IGNITION AS AN ESTIMATE OF TOTAL ORGANIC CARBON IN THE MOUNTAIN SOILS

Abstract. Due to the ease and low cost of implementation, a commonly used method of determining the humus content in soils is the loss-on-ignition (LOI) method. Several regression equations and transformation factors are reported for LOI conversion to soil organic matter (SOM) or total organic carbon (TOC) content. The vast majority of the conversion factors have been developed for surface horizons of lowland soils, while there are only few findings from the mountainous areas. 476 mineral and 79 organic (forest litter) samples from 31 soil profiles located in different altitude zones of the Karkonosze Mountains and under different vegetation were used for analysis. LOI was determined by the drying-weighing method and TOC by the dry combustion method with CO_2 absorption. The average LOI/TOC ratio was about 2, but varied in accordance to LOI value. At the LOI value above 8–10%, the LOI/TOC is maintained at a constant level of 2.0, but with a decreasing LOI it may significantly extend, up to 20 at LOI <1%. In the mountain soils, the best compatibility of TOC determined and estimated based on LOI was obtained when using different conversion factors (7.3, 5.0, 3.1 and 2.0) for the four LOI ranges (0–2, 2–4, 4–8, and > 8%, respectively) or when using separate regression equations for LOI of <8 and >8%. Because of huge TOC overestimation by LOI method at LOI values lower than 8–10%, the conversion LOI to TOC is not recommended, unless the direct measurement of TOC content is currently unavailable (e.g. in archival databases).

Carbon bound in the soil organic matter (SOM) is the largest pool of this element among all compartments of terrestrial environments. Soil organic carbon pool is estimated at 2500 Pg, and is nearly four times larger than the biotic and three times larger than atmospheric resources. Therefore, carbon circulation

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in the ecosystems has become a scientific topic receiving increasing attention, particularly in the context of long-term climate change [9, 6]. There are many methods for the determination of soil organic carbon and the coefficients for the conversion to organic matter [7]. Due to the ease and low cost, a common method is to determine the so-called loss-on-ignition (LOI), which is the percentage weight loss of the sample due to combustion at a temperature of at least 500–550°C [10, 14, 16]. The loss-on-ignition method, as the simplest and cheap, is still preferred in geological, geomorphological and archaeological studies [19]. However, the results of this analysis can be regularly or irregularly overstated for two reasons: (1) the release of CO_2 from carbonates and (2) the release of water bound in clay minerals. First threat can be eliminated relatively easily by the use of the combustion temperature below 500°C, or by prior dissolution of carbonates by sample treatment with hydrochloric acid. The second source of inconsistency depends on the kind and content of soil clay minerals and cannot be easily overcome [2]. Based on the LOI analysis it is possible to directly determine the total organic carbon (TOC) content in the soil using an appropriate correction coefficient [1]. Also, using the conversion factors or regression equations is necessary to standardize the various databases, containing data of the organic carbon content (organic matter) received by different analytical methods.

Most of the works on coefficients for the loss-on-ignition transformation to organic matter or organic carbon content was carried out in soils of lowlands, and there are very few such comparisons for mountain soils [1, 5, 7, 11, 18]. Meanwhile, both the mineralogy of the mountain soil (prevalence of primary minerals in the bedrock regolith), and the composition of soil organic matter (coming from spruce domination in the mountain forests), differ from these in the soils developed in lowlands, which may influence the loss-on-ignition. The aim of this paper is to determine the relationship between LOI and the total organic carbon content, and to determine the regression equations and conversion factors in samples of mountain soils with diverse organic matter content.

MATERIAL AND METHODS

476 mineral and 79 organic (forest litter) samples were collected in soil profiles at 31 sites located in the Karkonosze Mountains, in a wide range of altitudes (between 400 and 1400 m a. s. l.), and under different vegetation (arable lands, grasslands, beech stands, spruce stands, and mountain pine stands).

Samples from mineral horizons were collected by steel cylinders having a volume of 100 cm^3, and the organic samples – with a steel cylinder having a diameter of 18 cm. According to FAO-WRB classification [12] the soils belong to the following types and subtypes (in brackets – according to Systematics of

Polish Soils [15]): Stagnic Luvisols (gleby płowe opadowo-glejowe), Dystric Skeletic Cambisols (gleby brunatne dystroficzne typowe), Folic Albic Podzols (bielice typowe) and Histic Albic Podzols (stagnobielice). All soils are developed from granite regolith or colluvic materials, with a texture of loamy sand, sandy loam, or loamy silt. Soils do not contain carbonates and their reaction is acidic or strongly acidic throughout the profile [13].

In the collected samples, the loss-on-ignition (LOI) was measured by burning 5–10 g of soil (dried at 105°C to constant weight) in a muffle furnace at 550°C for 5 h, and the total organic carbon (TOC) by dry combustion with spectroscopic detection (NIR) of the released CO_2 using the CS-MAT analyzer (Ströhlein, Germany). Due to the lack of calcium carbonate in the soils, the total carbon content (as measured by dry combustion) is an equivalent to total organic carbon.

Basic statistical measures, e.g. arithmetic and geometric means, standard deviations have been calculated, and analysis of variance with Tukey's post-hoc test, at $p<0.05$, to check the statistical significance of differences between distinguished subgroups. Moreover, the Pearson's correlation coefficients and regression equations were calculated to describe the quantitative relations between LOI and TOC, both in entire database and in distinguished subgroups. All statistical calculations were performed using the STATISTICA 10 PL package.

RESULTS AND DISCUSSION

LOI values varied in a wide range from 0.93 to 92.1%, with the arithmetic mean of 13.4%, and the organic carbon content varied in the range from 0.09 to 50.8% (Table 1). Very high values of the standard deviation (exceeding the mean values almost twice), as well as significant differences between arithmetic and geometric values show high diversity of analysed soil samples. This is because the database involves a wide range of typically mineral and organic samples reflecting the diversity of the entire soil profiles. The distribution of the results (both TOC and LOI) is bimodal (Fig. 1a and 1b); however, it is a seeming result of the unequal ranges of distinguished classes. Distribution of the results is right-skewed, due to the many samples with low LOI values (2–4% and 4–6%) or very low TOC content (0–1% and 1–2%).

The correlation coefficient for the linear regression equation of the relationship between TOC and LOI was calculated based on the entire database (Fig. 2). Statistical analysis shows a very high degree of dependence ($R^2 = 0.97$, $p = 0.000$) and a linear trend described by regression equation: $y=0.52x-0.55$ (Table 2). Very good match of trend line (TOC predicted values) to the measured LOI values is visible in the graph (Fig. 2), particularly within the LOI range from 8–10 to over 90%. However, a number of results form an extensive cloud at the low LOI values (especially <8%), suggesting a poorer fit to the results calculated in this LOI range. In addition, a fairly large negative intercept in the regression equation means that the estimated TOC content falls below zero if the LOI value is less than 1%.

TABLE 1. RANGE, ARITHMETIC AND GEOMETRIC MEAN, STANDARD DEVIATION OF LOSS-ON-IGNITION (LOI) AND TOTAL ORGANIC CARBON (TOC) CONTENT THROUGHOUT SOIL DATABASE USED FOR ANALYSIS

Parameter	LOI [%]	TOC [%]
Range	0.93–92.1	0.09–50.8
Mean	13.36	6.43
Geometric mean	5.96	1.88
SD	21.60	11.45

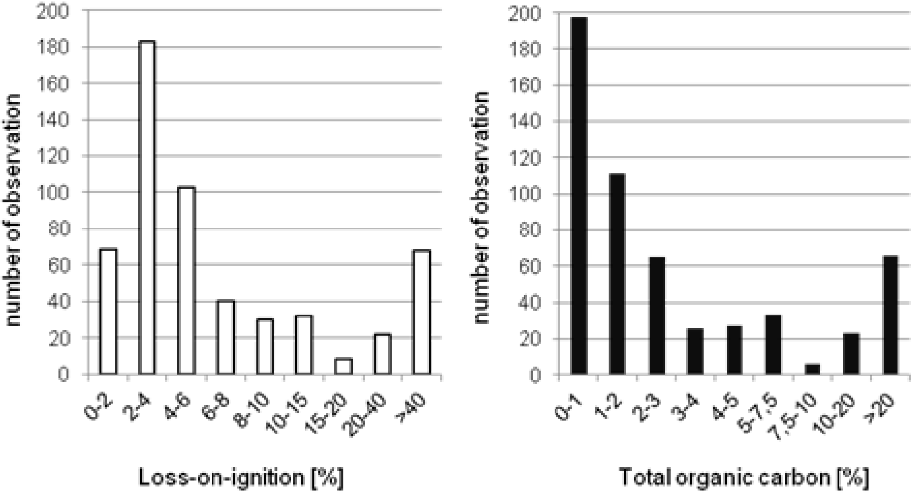

Fig 1. Distribution histograms of LOI value (1a) and TOC content (1b) in soils in the database used for analysis.

The regression equation indicates that at high LOI values, the LOI/TOC ratio is close to 2, which is illustrated by Figure 3. In turn, in the samples with a low content of organic matter (LOI <8%), where the intercept is relatively more influencing the linear regression equation, the LOI/TOC ratio may have much higher values, up to 20 or more (Fig. 3). It is obvious that the regression equation calculated for the entire database does not describe properly the relationship between loss-on-ignition and total organic carbon in this range of LOI; thus, the conversion coefficient 2 has a limited use in this case.

TABLE 2. REGRESSION EQUATIONS AND LOI/TOC CONVERSION FACTORS CALCULATED FOR ENTIRE DATABASE AND DISTINGUISHED SOIL CLASSES (DIFFERING IN LOI VALUE)

LOI range	Regression equation	Mean LOI/TOC conversion factor
All database	$y=0.52x-0.55$, $R^2=0.97$, $p<0.01$	n.d.
0–2%	$y=0.24x-0.09$, $R^2=0.12$, $p<0.01$	7.3[a]
2–4%	$y=0.42x-0.39$, $R^2=0.28$, $p<0.01$	5.0[b]
4–8%	$y=0.50x-0.53$, $R^2=0.41$, $p<0.01$	3.1[c]
>8%	$y=0.51x+0.02$, $R^2=0.94$, $p<0.01$	2.0[d]
0–8 %	$y=0.51x-0.61$, $R^2=0.72$, $p<0.01$	n.d.

Explanation: – [a, b, c, d] – homogeneous groups of mean values calculated by Tukey's multiple range test (significant at $p<0.05$), various superscripts indicate significant differences between mean values; n.d. – not determined.

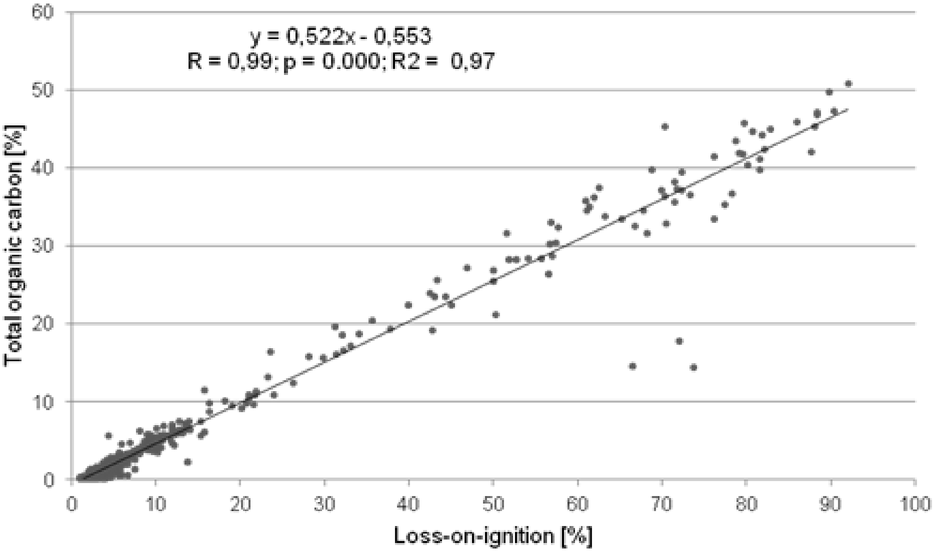

Fig 2. Linear regression equation and correlation coefficient for total organic carbon and loss-on-ignition (all samples).

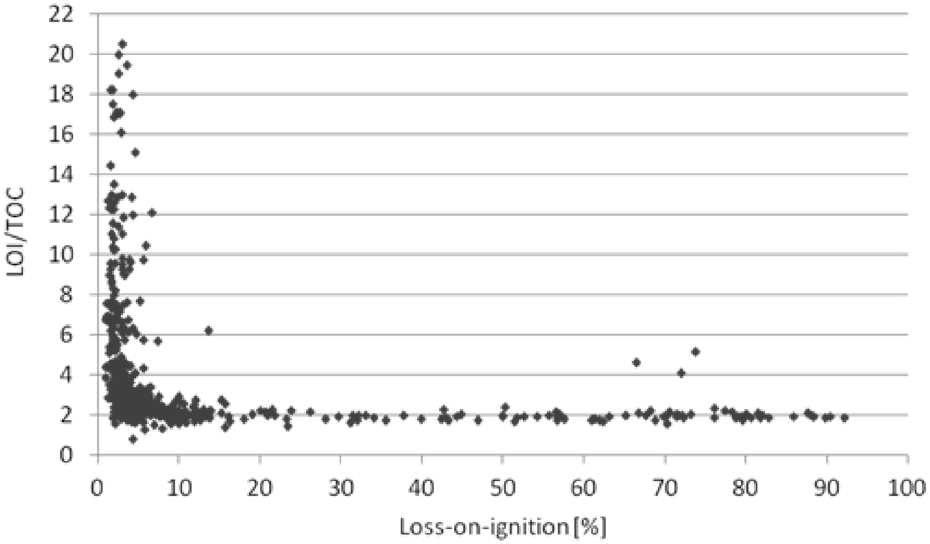

Fig 3. LOI/TOC ratio in relation to LOI values.

In order to find better approximation of the LOI/TOC relationship, the regression equations were calculated separately for soil that have LOI values below and above 8% (Table 2). The regression equation for the LOI >8% ($y = 0.51x + 0.02$) indicates a nearly proportional relationship between TOC and LOI (minimum intercept), which strongly justifies the application of the conversion factor 2. Correlation between LOI and TOC at the LOI values <8% is statistically weaker, but proves more than 70% of the results (Table 2). However, the intercept of the linear regression equation ($y = 0.51x - 0.61$) is even greater than in the equation based on the entire database, which means a greater risk of negative TOC calculated from LOI values <1%. Other tested non-linear regression equations (polynomial or logarithmic) did not give a better fit of the measured and calculated values of TOC and did not solve the problem of negative predicted TOC values in this LOI range.

Analysis of the LOI / TOC ratio for different ranges of organic matter content indicates that there are statistically significant differences (based on approximation using Tukey's test) between the mean values of the LOI / TOC ratio for the following LOI ranges: 0–2, 2–4, 4–8 and> 8% (Table 2). The highest mean values of LOI / TOC, about 7.3, are in the LOI range of 0–2% , but the maximum values of LOI / TOC (over 20), are in the next class (2 – 4% LOI), where the average value of LOI / TOC was estimated at 5.0. In the next class (4 – 8% LOI), the LOI/TOC index has an average value of 3.1. For the LOI range from 8 to 92%, as mentioned above, the LOI/TOC ratio of 2.0 was adopted. Values for the classes in the narrower LOI range (for example of 8–10, 10–20, 20–40, 40–60, and > 60% LOI) oscillate in the range of 1.85–2.1 and the differences between them are statistically insignificant.

Linear regression equations for each distinguished class of LOI (Table 2), although all statistically significant, have unequal practical usefulness (e.g. an equation for LOI values of <2% explains only 12% of the observations – $R^2=0.12$). However, their superiority over the regression equations based on a wider range of LOI is that they solve better the problem of negative predicted TOC values.

Although many researchers use the LOI method to determine SOM stocks, it is believed that this technique slightly overestimates SOM content and is sensitive to the influences of other soil components, such as calcium and magnesium carbonates, clay fraction and mineral-organic complexes [2], which may affect the amount of inorganic carbon or bound water. Direct conversion of LOI to TOC also reveals the doubts about the constant proportion of carbon in organic matter, traditionally defined to be 1.724 [5, 18]. As a result, many researchers indicate the need to use more than one conversion factor [11] or different regression equations, including nonlinear and multivariate regressions [5].

It appears that the estimation of TOC based on LOI values is more reliable in organic and mineral-organic soils containing more than 10% of organic matter. In the Indonesian peat, Farmer et al [7] found the appropriate value of the conversion factor LOI / TOC at 1.88. In turn, for litters of forest soils, Howard and Howard [11] have suggested a ratio of 2.0 (in the range from 1.5 to 2.5), and Száva-Kovats [17], based on a statistical compilation of various researchers, indicated proportions in the range of 1.6–2.1. Also in the highly organic bottom sediments [2] the most appropriate ratio is close to 2, although there is a need of subsequent correction due to the high content of clay fraction. These observations are consistent with the results from forest litters and mineral-organic horizons of the soils in the Karkonosze Mts., where the mean LOI/TOC coefficient oscillated in a narrow range around a value of 2 and did not refer to the content of organic matter (in LOI range of 8–92%) or other soil properties, and soil location.

The opinions are much more variable in the case of mineral soils. Wang et al. [18] for the soils of semi-arid zone of China, and Cresser et al. [5] for the soils of the temperate zone of Great Britain have suggested a regression equation, which approved the conversion factor oscillating in the range of 2.1–2.4, depending on the organic matter content, soil texture and the kind of pattern material. Analysing the soil with a wider range of LOI, Howard and Howard [11] indicate that the LOI / TOC ratio may rise up to 5.8. The observations of Christensen and Malmros [4] showed that the ratio can reach even 15.4 at a very low LOI value. These findings are in line with the observations of mineral soil horizons in the Karkonosze Mts., where the proportion of LOI/TOC reached up to 20 at low LOI values. These high LOI/TOC ratios in the soils of the Karkonosze Mts. are not the highest ever, as Szava-Kováts [17] has reported ratios even above 50. The LOI/TOC conversion factors 7.3 for soils with LOI <2% and 5.0 for soils with 2–4% LOI (and analogous linear regression equations), found in soils of the Karkonosze Mts., seem to be incredibly high and indicate excessive discrepancy between the result of LOI analysis and the actual content of the organic matter and organic carbon in soils (at low LOI).

The source of this discrepancy is not fully understood. Most authors point to the role of water bound in the structures of clay minerals and clay-mineral complexes that may preserve water even after drying the samples at 105°C [11, 1]. This phenomenon may be enhanced by a particularly high content of clay fraction [2]. Meanwhile, the soil of the Karkonosze Mountains are rather poor in soil clay fraction [13], thus this cannot be the source of such a large discrepancy. Also, the repetition of certain analyses and precise control of the measurement conditions allow eliminating the random laboratory errors as a source of discrepancy between LOI and TOC. It seems that the most likely cause of overestimation of organic matter in mountain soils by LOI method is water binding in the mineral-organic complexes. In particular, the amorphous iron oxides may form stable "residual" fraction of humus that is very common in mountain soils even at low SOM content [8]. Significant loss of the clay fraction mass related to the loss of bound water, was recorded by thermogravimetric method (DTA/DTG) in the temperature range of 150–200^{o}C in soils formed from granite by Bogda et al. [3].

Examination of mountain soils has confirmed that the LOI method can be successfully used for the direct estimation of organic matter and organic carbon in soils having the LOI value higher than 8–10%. However, with regard to the mineral soil, calculation of TOC based on the LOI measurement, either by using linear regression equations or conversion factors, may be used only for archival data when a more accurate method is unavailable [1, 7, 18].

CONCLUSIONS

The total content of organic carbon (TOC) in soils having more than 8–10% of organic matter is highly correlated with the loss-on-ignition (LOI) values and may be calculated from the LOI by using a regression equation ($y = 0.51x + 0.02$) or by dividing the LOI value by 2.

In the mineral horizons of mountain soils, the LOI/TOC proportion increases inversely to LOI value that eliminates any single LOI/TOC conversion factor for the entire spectrum of mineral soils.

Because of the high degree of TOC overestimation by the LOI method at LOI values lower than 8–10%, the conversion of LOI to TOC is not recommended, unless the direct measurement of the TOC content is currently unavailable (e.g. in archival databases).

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STRATY PRAŻENIA JAKO PODSTAWA WYLICZANIA CAŁKOWITEJ ZAWARTOŚCI WĘGLA ORGANICZNEGO W GLEBACH GÓRSKICH

Ze względu na łatwość i niskie koszty wykonania, bardzo często stosowaną metodą określania zawartości próchnicy w glebach jest oznaczenie strat prażenia. Podawane są różne równania regresji (lub współczynniki przeliczeniowe) strat prażenia na materię organiczną oraz węgiel organiczny. Zdecydowana większość współczynników przeliczeniowych opracowana została dla poziomów powierzchniowych gleb nizinnych, natomiast do rzadkości należą badania na obszarach górskich. W badaniach wykorzystano 476 mineralnych oraz 79 próbek organicznych (forest litter) z 31 profilów gleb położonych w różnych strefach wysokościowych Karkonoszy (od 400 do 1400 m n.p.m.) oraz pod różną roślinnością. Oznaczono straty prażenia (LOI) metodą suszarkowo-wagową oraz całkowitą zawartość węgla organicznego (TOC) przez spalanie na sucho w analizatorze CO_2. Przeciętna proporcja LOI/TOC wynosiła około 2, ale różniła się w poszczególnych zakresach zawartości materii organicznej. Przy stratach prażenia 8% i wyższych, wartość współczynnika LOI/TOC utrzymuje się na stałym poziomie 2, jednak w miarę zmniejszania się strat prażenia ulega znacznemu rozszerzeniu, nawet do 20 przy LOI<1%. Ze względu na możliwe przeszacowanie zawartości TOC w próbkach o LOI poniżej 8–10%, nie zaleca się konwersji LOI na TOC w takich próbkach, chyba że bezpośrednie oznaczenie TOC jest obecnie niemożliwe (np. w przypadku danych archiwalnych).