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Organic carbon content in soils of long-term field trial: comparison of analytical methods

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The purpose of this study was to compare two wet digestion methods, the Tyurin method and the Austrian guideline ÖNORM L 1081, for the determination of soil organic carbon (SOC). For this purpose the impact of conventional, integrated, organic and biodynamic farming systems on SOC content was determined. The efficiency of the wet oxidation methods was evaluated using the results obtained by high-temperature dry combustion. Organic carbon contents determined by the Tyurin method were higher than those from ÖNORM L 1081 or high-temperature combustion method. The Tyurin method overestimated the SOC content. The agreement between high-temperature dry combustion and the ÖNORM L 1081 results suggested that SOC in the investigated soil type and sampling horizon could be completely recovered by using wet digestion under conditions described. In the beginning period, no significant differences were observed between the farming systems under study. The results of this study, however, indicate that the choice of the analytical method is important for accurate determination of SOC content.

Key words: wet digestion, soil organic carbon, farming systems

INTRODUCTION

Organic matter in the world's soils contains about three times as much carbon as it is found in the world's vegetation. Soil organic matter, therefore, plays a critical role in the global carbon balance that is thought to be the major factor affecting global warming, or the greenhouse effect. Organic matter comprises only a small fraction of the total mass of most soils, but this dynamic soil component exerts a dominant influence on many soil physical, chemical, and biological properties (Brady and Weil 1999).

Changes in agricultural practices for the purpose of increasing SOC must either increase organic matter inputs to the soil, decrease decomposition of soil organic matter and oxidation of SOC, or a combination thereof (Follett 2001). These practices include, but are not limited to, reducing tillage intensity, decreasing or ceasing the fallow period, using a winter cover crop, changing from monoculture to rotation cropping, or altering soil inputs to increase primary production (e.g., fertilizers, pesticides, and irrigation). The long-term use of conservation tillage practices has been identified as a potential strategy for mitigation of C losses from agricultural soils (Paustian et al. 1997).

SOC content can be increased by greater biomass production and greater retention of crop residues through adoption of a diverse crop rotation and conservation tillage (especially no tillage) that retains crop residue on or near the soil surface (Lal 1998; Reicosky and Allmaras 2003). Changes in available crop residue, soil management, and technological inputs enable agriculture to reduce SOC losses (Johnson et al. 2006).

In any farming system, soil organic matter content changes towards an equilibrium value that depends on the quantity of added organic material, its rate of decomposition, the rate of the breakdown of existing humus, soil texture, and climate (Poulton and Johnson 1994).

The amount of carbon in European soils is estimated to be equal to 73 to 79 billion tones. Today, monitoring and knowledge on land use and land use change in EU27 is inadequate for accurate calculation of changes in soil carbon contents.

Several methods are available in the literature to determine organic carbon. Some methods are based on titration after wet oxidation of SOC, while the others use dry combustion at high temperatures followed by the detection of evolved CO_2 or the SOC content is determined by weight loss on ignition (Schumacher 2002). Since all methods available have some limitations, the choice of assessment methodology is a critical decision for accurate quantification of SOC content.

Environmental concerns regarding the considerable amounts of polluting wastes containing the toxic form of chromium (Cr^{6+}) favoured the use of dry combustion methods. Vibeke et al. (2003) reported on the draft harmonised standard based on high temperature combustion. The draft standard was proposed after detailed comparison of the two present standards ISO 10694 and EN 13137. The available standard ISO 14235 based on oxidation of SOC by potassium dichromate in the presence of sulphuric acid was not included due to already mentioned disadvantages.

The aim of the present paper was to compare two different wet digestion methods used for determination of total organic carbon content and to apply them to assess the impact of different farming systems on SOC content.

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MATERIALS AND METHODS

Sampling and sample preparation

The soil samples were taken in April 2010 from a field trial located in Hoče at the North East of Slovenia (46°28′N, 15°38′E, 282 m a.s.l). The soil is classified as dystric cambisol. Annual rainfall in the locality is approximately 1000 mm. The long time field trial was started in 2007 and consists of five different farming systems (control, conventional, integrated, organic and biodynamic). In one rotation there are typical crops for this region (two years of red-clover grass, wheat, white cabbage, oil pumpkins), the other one is an alternative crop rotation (two years of red-clover grass, spelt, red beet, false flax). Four production systems + control plots were arranged in a randomized complete block split-plot design with four replicates (Turinek et al. 2010). A total of 20 soil samples were collected (four replicates from each experimental field) in accordance with ISO/DIS 10381-1 Zig-Zag traverse sampling pattern. The preceding crop on the sampled plots were oil pumpkins, which were harvested in autumn 2009. The sampling depth of 0.2 m was chosen, because this is the depth to which organic carbon in soils is most likely to be affected by land use change (Woomer et al. 2001). The air dried soil samples were ground using a soil mill (Cross beater mill, SK100/C Spezialstahl, Retsch) and sieved to pass through a 1 mm sieve (according to Tyurin method) or 2 mm sieve (ÖNORM L 1081).

Reagents

All reagents used were of analytical reagent-grade. Deionised water of 18 MΩ/cm resistivity purified with Milli-Q system (Millipore, Bedford, USA) was employed throughout.

Analyses of soil organic carbon

For each sample, the SOC content was determined by using two methods: (1) the Tyurin titrimetric method and (2) the Austrian guideline ÖNORM L 1081, better known as the method of Walkley and Black (1934) which was modified to include external heating of sample during digestion.

Tyurin titrimetric method: Appropriate quantity of soil sample was weighed into an Erlenmeyer flask. Twenty grams of potassium dichromate ($K_2Cr_2O_7$) were dissolved in 400 ml of distilled water, 500 ml of concentrated H_2SO_4 was added, and then the solution was diluted to the final volume of 1L. Ten milliliters of the prepared solution was added to the soil sample and the flask was heated 20 min at 150 °C. After oxidation of soil organic matter (Equation 1), unused potassium dichromate was titrated with a standard solution of ammonium ferrous sulphate (Equation 2). The obtained results were multiplied by correction factor of 1.17.

Equation (1)

$$3C+2K_2Cr_2O_7+8H_2SO_4 \rightarrow 3CO_2+2Cr_2(SO_4)_3+2K_2SO_4+8H_2O$$

Equation (2)

$$6FeSO_4+(NH_4)_2SO_4+K_2Cr_2O_7+7H_2SO_4 \rightarrow Cr_2(SO_4)_3+3Fe_2(SO_4)_3+6(NH_4)_2SO_4+K_2SO_4+7H_2O$$

The Austrian guideline ÖNORM L 1081: Soil sample was treated with 10 mL of 0.167 mol/L $K_2Cr_2O_7$ solution in the presence of concentrated H_2SO_4 as described by Walkley and Black (1934). During digestion the flask was heated under conditions described in ÖNORM L 1081. Excess dichromate was titrated with ferrous sulphate solution. The end point of the titration was recorded based on visual colour change and the percentage of SOC calculated. Triplicate measurements were made on blank solution and on each individual sample.

The soil samples taken in the control field and in the field with integrated soil management were also analysed by total organic carbon analyzer (TOC-analyzer). The sample was heated to 900 ˚C in the flow of oxygen-containing gas and the evolved CO_2 was measured. Measurements were performed according to ISO 10694. The SOC content was obtained as the difference between the total carbon and inorganic carbon content.

The percent recovery obtained by the Tyurin method and the ÖNORM L 1081 compared to dry combustion method was calculated by dividing SOC content (%) by the Tyurin method or ÖNORM L 1081 with the SOC content obtained by dry combustion and multiplied by 100.

Table 1. Comparison of soil organic carbon contents determined by the Tyurin method, the ÖNORM L 1081 and dry combustion method for different farming systems

System	Average of SOC (%)		
	Tyurin	ÖNORM L 1081	TOC analyzer
Control	1.80±0.17	1.53±0.14	1.50
Biodynamic	1.82±0.14	1.58±0.09	/
Conventional	1.85±0.11	1.59±0.05	/
Organic	1.79±0.19	1.57±0.18	/
Integrated	1.82±0.07	1.57±0.10	1.50

No statistically significant differences were found between the farming systems. Each data point represents the mean value ± standard deviation (SD from three replicate measurements on each sample from four field replications in each system).

Statistical analyses

The obtained data were analyzed using MS Excel 2003© and SPSS version 14.0 for Windows (SPSS. Inc., Chicago, IL). Analyses of variance (ANOVA) were performed on data for SOC contents of different farming systems and means were compared by Duncan's test ($P \leq 0.05$). The homogeneity of variances was tested by Cochran's C test. A comparison of both methods was done using a simple regression procedure by fitting the data to a linear model.

RESULTS AND DISCUSSION

A comparison between the methods used for organic carbon determination

The basic principle of both methods, which are based on wet oxidation is the oxidation of soil organic matter with acidified potassium dichromate and the estimation of the amount of potassium dichromate used for organic matter oxidation. The variations between the methods existed in the concentration of $K_2Cr_2O_7$ solution, in the combination of reagents used, and in the oxidation conditions (heating time and temperature). The principle of wet oxidation is essentially the same to the one described in ISO 14235. The difference between the methods is in quantification which relays on titration (Tyurin and ÖNORM L 1081) or spectrophofotometry (ISO 14235 and ÖNORM L 1081). The Tyurin method traditionally has been and continues to be used for determination of SOC content in the mineral soils of East European countries.

The results obtained by the Tyurin method were corrected using a factor 1.17 to account for the incomplete oxidation of organic carbon. Organic carbon contents from the Tyurin method were higher in all investigated soil samples than those obtained by the ÖNORM L 1081 (Table 1). The mean values of SOC content in the 0.0-0.20 m horizon varied from 1.79 % to 1.85 % analyzed by Tyurin method and from 1.53 % to 1.59 % analyzed by the ÖNORM L 1081. The values of SOC content between the two methods are in a positive linear correlation (Figure 1). The correlation coefficient equals 0.787, indicating a significant, moderately strong relationship between the variables. Also when the two methods are compared without the correction factor of 1.17 in the Tyurin method, the correlation coefficient stays the same Table1, Figure1.

The results obtained by the ÖNORM L 1081 were in good agreement with those determined by the TOC-analyzer for both samples analyzed. SOC recovery was 101% and 105%, while using the Tyurin method the recoveries were 120% and 121%. Chacón et al. (2002) assumed that dry combustion using TOC analyzer enables an accurate measurement of SOC content. From the results obtained in our study it can be concluded that the procedure following the ÖNORM L 1081 gave accurate results in the soil samples investigated, while the Tyurin method overestimated SOC content. This overestimation was due to the use of correction factor of 1.17 with which the values obtained following the Tyurin procedure were multiplied. When external heat is applied during wet digestion of soil samples a complete digestion of SOC in the samples is achieved, and therefore no correction factor is needed (Anderson and Ingram 1993; Schumacher 2002).

Meersmans et al. (2009) suggested that note should be made on small differences in the methodology (the volume of potassium dichromate used or time/temperature of the oxidation reaction) which can have an important impact on the obtained SOC content. However, the evaluation of the results presented in this study showed that small differences in the methodology between the two wet digestion procedures, the Tyurin method and ÖNORM L 1081, used in this study,

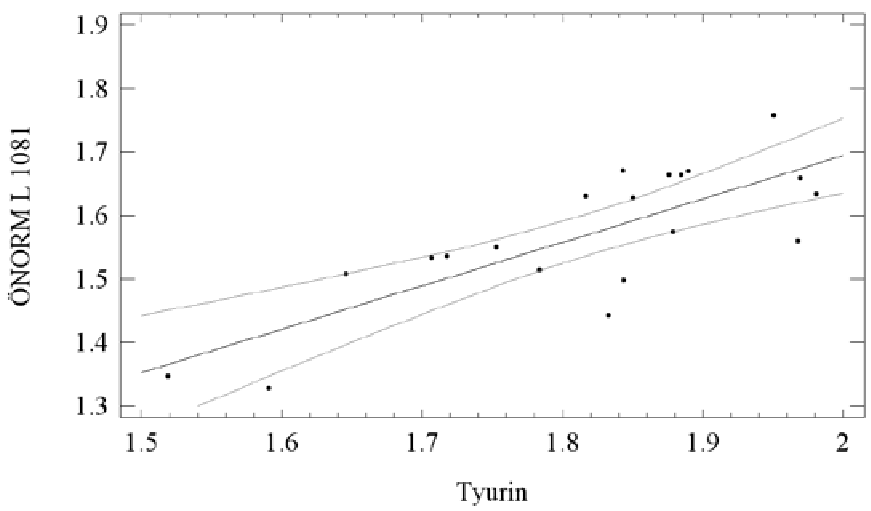

Fig. 1: Linear model of a regression analysis comparing the Tyurin method and the ÖNORM L 1081 method, with confidence limits set at 95% confidence level

The R^2 statistic indicates that the model as fitted explains 61.89% of the variability in ÖNORM L 1081. The correlation coefficient equals 0.787, indicating a moderately strong relationship between the variables.

did not have an important influence on the obtained organic carbon content in the investigated soil samples.

Chatterjee et al. (2009) reported that automated dry combustion is the only reliable method to determine SOC content in soils, but based on our results we could conclude that the procedure described in the ÖNORM L 1081 and the Tyurin method, without using the correction factor, both gave results that are in very good agreement with the dry combustion method and that they could give reliable results as well. Determination of SOC by dry combustion has been recognized as a standard procedure for the determination of SOC (Vibeke et al. 2003), however, many laboratories are still using wet oxidation because the TOC analysers are expensive and therefore they are not so commonly available in many laboratories.

The role of land use

Results from the Tyurin method show no statistically significant differences between the farming systems (Table 1). Among the five farming systems studied, the SOC content determined with the Tyurin method decreased in the order conventional > integrated > biodynamic > control > organic. Soils contained 'high' quantities of carbon according to the existing classification system based on the Tyurin method (1966).

Data obtained by the ÖNORM L 1081 again showed no statistically significant differences between the farming systems (Table 1).

The impact of different farming systems on SOC content was investigated in some other studies. Dou and Hons (2006) reported on loss of soil organic matter by intensive tillage systems, while in the study of Sombrero and Benito (2010) 30% higher values of SOC content were found at the depth of 10-20 cm with no tillage than with conventional tillage system. Significantly higher SOC content in organic farming system compared to the conventional one after twelve years long experiment was found by Heczko and Zaujec (2009). Results obtained by Tobiašová and Šimansky (2009) and by Szombathová (2010) suggested a higher soil carbon sequestration in the organic respect to the conventional system in a 6 years long experiment. In our study no significant differences were observed in SOC content between conventional, biodynamic or organic farming systems. This might be due to the fact that the experiment runs only three years, while in the cited references the increased SOC content was observed at the end of long term field experiments.

CONCLUSION

SOC content was determined by two wet oxidation methods which are commonly used in soil testing laboratories. The agreement between dry combustion and the ÖNORM L 1081 results suggested that SOC could be completely recovered by using wet digestion under conditions described. However, it should be taken into account that results obtained by different methods will depend on soil type, soil depth and mineralogy. Organic carbon contents from the Tyurin method were higher than those from the ÖNORM L 1081 or dry combustion, so the use of correction factor of 1.17 should be avoided when external heating is applied to the system during sample digestion.

Results obtained by ÖNORM L 1081 and the Tyurin method showed no significant differences between the farming systems. SOC content is one of the parameters used for the evaluation of soil quality, but its changes can only be assessed in long-term experiments when the same agricultural practices are run year after year. In our study the experiment was running 3 years and the results indicated that this period is probably too short to evaluate the impact of farming management on SOC content.

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