Comparison of Methods for Soil Sampling and Carbon Content Determination

Željka ZGORELEC [1](✉)[1], Milan MESIĆ[1], Ivana VUKOVIĆ [1], Aleksandra JURIŠIĆ [1],
Branka KOMESAROVIĆ [2], Domagoj KLAIĆ [3], Ivica KISIĆ [1], Ferdo BAŠIĆ [1], Krunoslav SAJKO [1]

Summary

In this paper methods for sampling and analysis of total carbon in soil were compared. Soil sampling was done by sampling scheme according to agricultural soil monitoring recommendations. Soil samples were collected as single (four individual probe patterns) and composite soil samples (16 individual probe patterns) from agriculture soil. In soil samples mass ratio of total soil carbon was analyzed by dry combustion method (according to Dumas; HRN ISO 10694:2004) in Analytical Laboratory of Department of General Agronomy, Faculty of Agriculture University of Zagreb (FAZ) and by oxidation method with chromium sulfuric acid (modified HRN ISO 14235:2004) in Analytical laboratory of Croatian Center for Agriculture, Food and Rural Affairs, Department of Soil and Land Conservation (ZZT). The observed data showed very strong correlation (r = 0.8943; n = 42) between two studied methods of analysis. Very strong correlation was also noted between different sampling procedures for single and composite samples in both laboratories, and coefficients of correlation were 0.9697 and 0.9950 (n = 8), respectively.

Key words

chromium sulfate oxidation, dry combustion, monitoring, soil sampling, soil carbon

[1] University of Zagreb, Faculty of Agriculture, Department of General Agronomy,
Svetošimunska cesta 25, 10000 Zagreb, Croatia
✉ e-mail: zzgorelec@agr.hr
[2] Croatian Center for Agriculture, Food and Rural Affairs,
Department of Soil and Land Conservation, Brijest-Usorska 19, 31000 Osijek, Croatia
[3] Gisdata, Baštijanova 52a, 10000 Zagreb, Croatia

Introduction

The determination of total carbon (TC) and total organic carbon (TOC) is an essential part of any site characterization or ecological assessment since its presence or absence can markedly influence how chemicals react in the soil or sediment. Numerous methods are available for the determination of TC and TOC in soils and sediments, some of them are laboratory and some are *in situ* methods (Chatterjee et al., 2009). Carbon can be present in elemental (TC), inorganic (TIC), or organic (TOC) forms. Carbon is usually derived from weathering of parent material/ geology, decomposition of plant and animal matter, or by addition through anthropogenic activities. There are numerous laboratory methods and variations of methods for identification and quantification of TC and TOC. These methods may be qualitative, semi-quantitative, or quantitative depending upon the technique used. Quantitative methods generally involve some form of sample preparation to remove water and/or inorganic carbonates, where present. After completing the sample preparation, either wet chemistry digestion or dry combustion techniques are used to convert the organic matter in the sample to CO_2, which is then quantified. Quantification techniques range from simple gravimetric determinations through volumetric and manometric measurements through the more complex spectrophotometric and chromatographic methods (US-EPA, 2002).

The aim of this research was to compare two methods for soil carbon determination, widely used in Croatia: wet and dry combustion methods used in two different laboratories. The second objective was to compare different soil sampling methods (single and composite).

Material and methods

Investigation was done at agriculture soil near village Potok in central Croatia on stationary field experiment established fifteen years ago. Soil type was Plain Pseudoglay (Škorić et al, 1985) or Stagnosol (FAO, WRB, 2006). Research Stations differed in N fertilization levels. Four Stations included treatments with: 0 kg N/ha, 150 kg N/ha, 300 kg N/ha and black fallow. Soil profile was taken and also included in investigation (Figure 1). Soil sampling was done by sampling scheme (Figure 2) according to agricultural soil monitoring recommendations (Mesić et al., 2006). Soil samples at each Station were collected as single (four individual probe patterns) and composite soil samples (16 individual probe patterns) at two depths: 0 cm - 37 cm (P) and 37 cm - 74 cm (Btg), what in total amounted to 10 soil samples at each Station. In all soil samples mass ratio of total soil carbon was analyzed using dry combustion method (according to Dumas; HRN ISO 10694:2004) in Analytical laboratory of Department of General Agronomy, Faculty of Agriculture University of Zagreb (FAZ) and oxidation method with chromium sulfuric acid (modified HRN ISO 14235:2004) in Analytical laboratory of Croatian Center for Agriculture, Food and Rural Affairs, Department of Soil and Land Conservation (ZZT).

Principle of dry combustion method

The carbon present in the sample (200 mg) is oxidized to CO_2 by heating the sample in oxidation column to a temperature of at least 900°C (any carbonates present are completely decomposed) in a flow of oxygen-containing gas. The amount of CO_2 released is then measured with thermal conductivity detector (TCD).

Figure 1. Monitoring Stations included in investigations
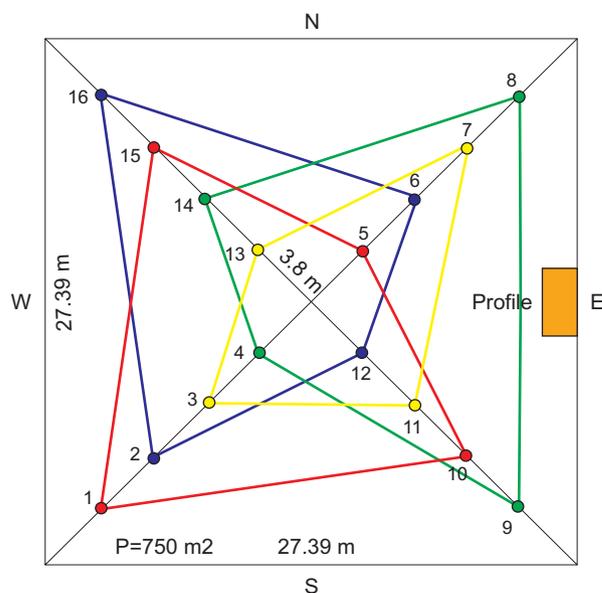

Figure 2. Soil sampling monitoring scheme

Mass ratio [g/kg] of total carbon (TC), total organic carbon (TOC) and organic mater (OM) in soil can be obtained from this method. Total organic carbon mass ratio can be measured by direct determination if carbonates are removed beforehand (sample treated with 4M HCl) and/or by indirect determination if we know $w(CaCO_3) \equiv w(TIC)$, by using a very simple calculation. Calculation equation is: $w(TOC) = w(TC) - [0.12 \times w(CaCO_3)]$, therewith, all mass ratios are on the basis of oven-dried sample (DM) and the conversion factor is 0.12. Organic matter mass ratio can be calculated if $w(TOC)$ is known. The equation for calculation is as follows: $w(OM) = [f \times w(TOC)]$, where f is a

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conversion factor, which depends on the type of OM and for agricultural soils may vary between 1.7 and 2.0 (usually, f=1.7241).

Principle of wet combustion method

The organic carbon present in the sample (1 g of sample) is oxidized in a mixture of dichromate solution ($K_2Cr_2O_7$) (30 mL; 1M solution) and H_2SO_4 (20 mL; concentrated acid) at a temperature of 135°C (heating block), so called:"wet combustion method". The dichromate ions $Cr_2O_7^{2-}$ [Cr^{6+}] (orange-red solution) are reduced to Cr^{3+} (blue - green solution). The intensity of blue-green color is measured spectrophotometrically (at λ =585 nm). The oxidation of one carbon atom of OM produces four electrons (to CO_2), so there is direct relation between Cr^{3+} formed and the amount of OC. Calibration was done using glucose ($C_6H_{12}O_6$, which is readily oxidizable carbon). Chemical equation of this extraction procedure is as follows: $2Cr_2O_7^{2-} + 3 C^0 + 16H^+ = 4Cr^{3+} + 3CO_2 + 8H_2O$ (US-EPA, 2002). The limitation of this method is that the reaction could not be quantitative and is not applicable, if the solid contains mineral reducing compounds (such as Cl^- or Fe^{2+}) in concentrations higher than ~ 0.4%-0.5% of analyzed sample.

Mass ratio [g/kg] of organic mater and total carbon in soil can be obtained by this method. Total carbon content can be calculated from w(OM). Calculation equation is as follows: w (TC) = [f × w (OM)], where f is a conversion factor, which depends on the type of OM (usually, f = 0.58 = 1/1.7241).

Results and discussion

The results of the comparison of total soil carbon [TC, %] content done by two different investigated methods in two different laboratories; dry combustion (FAZ) and wet combustion (ZZT) are shown in Figure 3. The observed data showed very strong positive linear correlation (r = 0.8943; n = 42) according to Roemer-Orphal scale (Vasilj, 2000) between two studied methods of analysis. Determined linear regression equation (functional dependence) is $TC_{FAZ}=1.163 \times TC_{ZZT} -0.1838$. In Australia, Kerven et al., 2000 compared three methods including the Wakley and Black and the Heanes methods (dichromate oxidation) and automated dry combustion method. Three methods showed good agreement between the Heanes method and the combustion method and only slightly lower recoveries by the Walkley and Black procedure. The measurement of carbon in soils by high temperature combustion in an oxygen atmosphere has been shown to be a rapid and reliable method capable of producing results in good agreement with one of the established dichromate oxidation procedures. The correlation of
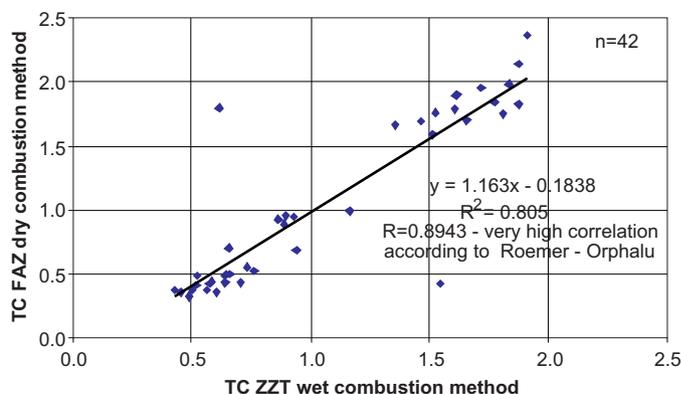

Figure 3. Comparison of methods for analysis of total soil carbon; dry combustion (FAZ) versus wet combustion (ZZT)
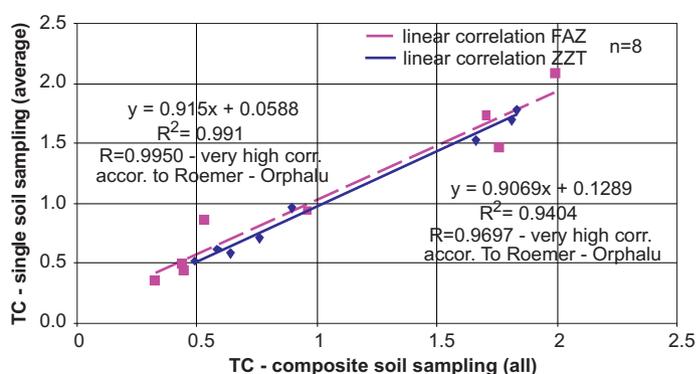

Figure 4. Comparison of soil sampling methods for total carbon content in soil, single versus composite measured in two different laboratories (FAZ and ZZT)

two different soil sampling methods is shown in Figure 4. Single soil sampling method (included four individual probe patterns) versus composite soil sampling method (included 16 individual probe patterns) measured in two different laboratories (FAZ and ZZT). Average value of total soil carbon content of four single soil samples for each soil depth is on the Y axis, each Station and each laboratory is shown (n=8), and total soil carbon content in composite soil samples for each soil depth is on X axis, each Station and each laboratory (n=8). Very strong positive linear correlation was also noted between total soil carbon content for

Table 1. Mean total carbon content in agriculture soil, depending on the N fertilizer rates at two investigated depths

Station	Depth	All – Monitoring		Single/average– Average (n=4)		Mean all	STD	RSD
		ZZT	FAZ	ZZT	FAZ			
Control	0-37	0.89	0.96	0.96	0.94	0.94	0.0313725	3
Control	37-74	0.49	0.32	0.52	0.36	0.42	0.0964786	23
300 kg N	0-37	1.83	1.99	1.78	2.09	1.92	0.1426265	7
300 kg N	37-74	0.64	0.43	0.58	0.50	0.54	0.091372	17
150 kg N	0-37	1.66	1.70	1.53	1.74	1.66	0.0911734	6
150 kg N	37-74	0.59	0.44	0.62	0.44	0.52	0.0932946	18
Black fallow	0-37	1.81	1.75	1.70	1.47	1.68	0.1482815	9
Black fallow	37-74	0.76	0.53	0.71	0.87	0.72	0.1427056	20

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different sampling procedures for single and composite soil samples in both laboratories, and coefficients of correlations were r=0.9697 and r=0.9950, respectively, (n = 8). Linear regression equations (functional dependence) are for two different laboratories, FAZ and ZZT, $TC_{single}=0.9069 \times TC_{composite} +0.1289$ and $TC_{single}=0.915 \times TC_{composite}+0.0588$, respectively.

Mean total carbon content in agriculture soil calculated as average value of single soil samples and composite soil samples obtained in both laboratories, depending on the N fertilizer rates at two investigated depths, and other parameters of descriptive statistic (standard deviation [std], relative standard deviation [RSD], minimal value, maximal value) are shown in Table 1. Mean total carbon content in agriculture soil (n=4) varied depending on the N fertilizer rates and investigated depths and was the highest (1.92% or 19.2 g/kg) in the surface layer (0 cm-37 cm) at Station (treatment) with 300 kg N/ha applied, and the lowest (0.42% or 4.2 g/kg) in the subsurface layer (37 cm-74 cm) at control Station (treatment) with 0 kg N/ha applied.

Conclusion

Very high correlation between two different investigated methods for TC determination in two different laboratories was determined (r=0.8943; n=42).

Both methods (dry and wet combustion) are valid and appropriate for agriculture measurements of TC on investigated soil type (Stagnosol).

Very high correlation between two different sampling methods (single versus composite) was recorded in both laboratories for TC and was (r=0.9950; n=8) in ZZT and (r=0.9697; n=8) in FAZ.

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