POLISH JOURNAL OF SOIL SCIENCE
VOL. XLVIII/1 2015 PL ISSN 0079-2985

DOI: 10.17951/pjss/2015.48.1.47

Soil Chemistry

GABRIELA BARANČÍKOVÁ*, JARMILA MAKOVNÍKOVÁ**

COMPARISON OF TWO METHODS OF SOIL ORGANIC CARBON DETERMINATION

Abstract. Soil organic carbon (SOC) is one of the basic soil parameters which takes part in many biological, chemical and physical soil processes and the SOC is currently considered as a key indicator of soil quality. For this reason determination of the SOC is a part of soil complex monitoring which has been performed in Slovakia since 1993. From 1993 until 2007 the "wet" method of determination of the SOC was used. Since 2008 the "dry" method for determination of the SOC has been applied. The goal of this work has been to evaluate and compare two methods of the SOC determination; the "wet"(Ťiurin method in modification of Nikitin (TN)) and the "dry" determination of the SOC by means of the CN analyser (EA), which was performed on 95 soil samples of topsoil coming from 17 sampling sites with a wide range of the SOC (1–15%). Sampling sites include arable lands and grasslands and represent main soil types and subtypes of Slovakia. On the basis of statistical processing it has been found that in soils with the SOC content up to 3%, differences between two methods are minimal. However, in the case of a higher content of the SOC, the EA method reaches a higher value than the TN method. Obtained data shows that in the case of soil samples with a higher content of the SOC, when changing an analytical method, the PTF function that reduces differences and allows to use all time series monitoring data should be used for the purpose of the tracking trends of the SOC monitoring.

The soil organic carbon (SOC) participates in many biological, chemical and physical soil properties. For this reason the SOC is one of basic parameters of soil fertility and it also influences non-production soil functions. The soil organic carbon currently is a key indicator of soil quality [11]. The Directive of the European Community [2] defines the soil organic carbon reservoir among

---

* Prof. G. Barančíková, DSc., National Agricultural and Food Centre – Soil Science and Conservation Research Institute, Regional Station, Raymannova 1, 08001 Prešov;

** Prof. J. Makovníková, DSc., National Agricultural and Food Centre – Soil Science and Conservation Research Institute, Regional Station, Mládežnícka 36, 97404 Banská Bystrica, Slovakia.

priority soil functions. The SOC is the main component of the soil organic matter (SOM). The SOM, depending on conditions, is capable of eliminating or sequestrating greenhouse gas fluxes in the natural environment. At present, one of the main threats in the EU countries is the reduction of the soil organic matter stock [14]. For this reason, determination of the soil organic carbon is an important part of the complex soil monitoring which has been performed in Slovakia since 1993. Within the framework of the basic monitoring network, which represents all main soil types, geological parent materials, climatic regions, soil management (arable soil, grassland) in 318 monitoring localities on agricultural and alpine soils, the basic parameter of the soil organic matter – the soil organic carbon in topsoil (at the depth of 0–10 cm) and subsoil (at the depth of 35–45 cm) is determined. Within the monitoring framework, apart from the basic network, there also exists the network of key monitoring sites, which involves 31 monitoring sites and it serves the purpose of soil monitoring in one year interval as well as the purpose of verification of new monitoring methods [5].

Ever since the 30's of the last century the worldwide known method of determination of organic carbon by means of soil oxidation with strong oxidizer has been used. The most widely and the most frequently used one, mainly in west European countries, is the Walkley & Black method [15] because it is simple and relatively quick. The principle of this method is oxidation of the soil organic carbon with excess dichromate in a concentrated sulfuric acid. The amount of oxygen consumed for oxidation of the soil organic carbon is determined by the difference between the non-consumed and consumed amount of dichromate. Non-consumed potassium dichromate is determined by redox titration with ferrous ammonium sulphate.

In Russia and east and middle Europe determination of the soil organic carbon by the Ťurin method was used [6]. In principle the Ťurin method is the same as the Walkley-Black method but soil sample with potassium dichromate is inserted at some time in the oven at 160^0C. There are several variations of time and temperature of heating [6,13]. It should be noted that by means of this method, quantitative determination of the SOC only in soils with the percentage share of carbon up to 15% is possible. At higher values of the soil organic carbon, determination of the SOC is incomplete [15] and thus this method is not suitable for the SOC determination in organosols or peats.

In the 80's of the last century the "dry" method of the SOC determination by means of automated CHN(OS) apparatuses started to be used worldwide. This method is based on thermal oxidation of soil sample at about 1000^0C. Carbon dioxide that is released is identified by suitable detectors; by means of a gas chromatography or infrared analysis [1]. By means of the CHN equipment total carbon is determined because at this temperature organic and inorganic carbon is decomposed. If only organic carbon do we need to measure from soil sample, carbonates are removed before determining the sample in an analyser [12] or total carbon is determined and content of organic carbon is calculated on the basis of the total carbon after correction for carbonates [1]. Determination of the soil organic carbon by means of the CHN analyser is much more expensive in comparison to the “wet method”, however it is more accurate, faster, requires a minimum sample and very often in the soil other biogenic elements may also be determined [12]. Within the framework of the soil monitoring, the soil organic carbon was determined according to the Ťurin in Nikitin modification from 1993 until 2007 and since 2008 the SOC has been measured by means of the CN analyser. In order to evaluate the concentration of the SOC from previous cycles (1993, 1997, 2002) with the current ones (2007, 2013), respectively, future measurements it was necessary to statistically evaluate two methods of determination. The aim of this work is to evaluate and compare both methods of the SOC determination, which was performed on soil samples representing all main soil types and subtypes of Slovakia, with a wide range (1 – 15 %) of the soil organic carbon content.

MATERIALS AND METHODS

Methods of soil organic carbon determination

In the Soil Science and Conservation Research Institute from the beginning of 80’s of the last century until 2007 the SOC determination had been performed according to the Ťiurin method in Nikitin modification [3]. The principle of this method is the same as the Walkley-Black or the Ťurin: oxidation of soil organic carbon with excess potassium dichromate in a concentrated sulphuric acid. The amount of oxygen consumed for oxidation of the soil organic carbon is determined based on the difference between the non-consumed and consumed amount of dichromate. In contrast to the classical Ťurin method, in which non-consumed potassium dichromate is determined by redox titration with ferrous ammonium sulphate, at Nikitin modification Cr^{3+}, which was formed by the reduction of Cr^{6+} of potassium dichromate, spectrophotometrically at □=590 nm is determined [3]. Within the framework of the soil monitoring of Slovakia from 1993 until 2007 this method for determination of the SOC was used. Since 2008 in the Soil Science and Conservation Research Institute total carbon has been determined by means of the analyser Euro EA 3000 in the CN configuration, on the basis of which, after correction on carbonates, organic carbon content is calculated [1]. The principle of this method is combustion of soil sample in oxygen atmosphere. After removal of interfering gases, mixture is separated by means of a chromatography column using a thermal conductivity detector. Since 2008 for the purpose of the soil monitoring of Slovakia this method of the soil organic carbon determination has been used. The exact procedure of the “wet method” and “dry method” is an integrated procedure of soil analyses. [1]. In the case of both methods, soil samples were sieved through the 0.125 mm sieve.

Soil samples

95 samples from top soil (at the depth of 0–10 cm) of 17 sampling sites were used for the purpose of the SOC determination by means of both methods. 13 samples come from key monitoring sites on arable land and grassland. The set of samples was supplemented with 4 samples from the basic monitoring network on grassland because key monitoring sites are located mainly on arable land with low soil organic carbon content. Soil samples of key monitoring sites were sampled in 2001 and 2007–2012. Soil samples of the basic monitoring network were sampled in 2007 and 2012. The sampling set represents main soil types and subtypes and they cover a wide range of the SOC content (1–15%) and other soil parameters. In the case of analysed soil samples, all the soil parameters which are measured within the soil monitoring framework were determined [5]. Basic characteristics of sampling sites (2001) are found in the Table 1.

TABLE 1. BASIC SOIL PARAMETERS OF SAMPLING SITES

Locality	Soil types	Soil management	pH/KCl	$CaCO_3$ (%)	Clay fraction (≤0,01 mm) (%)
1	Haplic Fluvisol (Anthric, Calcaric, Siltic)	AL	7.38	12.0	39.4
2	Haplic Stagnosol (Siltic, Eutric)	G	4,86	0.75	39.2
3	Haplic Stagnosol (Siltic, Eutric)	AL	6.56	0.50	42.1
4	Haplic Chernozem (Anthric, Siltic)	AL	7.36	1.25	39.3
5	Haplic Cambisol (Skeletic, Dystric, Siltic)	G	4.62	0.01	39.2
6	Cutanic Luvisol (Anthric, Siltic, Abruptic, Hypereutric	AL	6.46	0.75	39.1
7	Haplic Fluvisol (Anthric, Eutric, Siltic)	AL	4.96	0.50	66.0
8	Haplic Arenosol (Dystric)	AL	4.32	0.02	6.1
9	Endofluvic Chernozem (Anthric, Siltic)	AL	7.43	18.8	43.9
10	Haplic Cambisol (Skeletic, Dystric, Siltic)	G	3.63	0.05	28.1
11	Leptic Umbrisol (Skeletic, Dystric)	G	3.37	0.50	31.7
12	Cambic Rendzic Leptosol (Skeletic, Eutric, Calcaric)	G	6.01	3.00	34.9
13	Umbric Andosol (Skeletic, Siltic, Dystric, Thixotropic)	G	4.15	0.50	27.4

14	Andic Umbrisol (Skeletic,Siltic)	G	5.13	0.25	44.6
15	Haplic Cambisol (Eutric,Siltic, Calcaric, Skeletic)	G	5.96	5.75	46.7
16	Mollic Rendzic Leptosol (Calcaric, Eutric, Skeletic)	G	7.01	3.25	63.7
17	Haplic Cambisol (Siltic,Dystric,Skeletic)	G	3.88	0.25	35.1

AL – arable land G – grassland

Statistical methods of processing

For the purpose of the data analysis correlation and regression analyses, the STATGRAPHIC Centurion XVII program was used. For the purpose of comparison of both methods, the related analytical data from sampling in 2001 and 2007–2011 (n=78) was used. Analytical values from sampling in 2012 (n=17) were used for the purpose of verification of the proposed pedotransfer functions [10].

RESULTS AND DISCUSSION

As it has been mentioned above, determination of the soil organic carbon is one of basic soil parameters which are regularly measured within the soil monitoring framework. From the beginning of monitoring until 2007 the SOC had been determined by means of the “wet method” and since 2008 the “dry method” has been applied.

For the purpose of the long-term monitoring of the soil organic carbon, the change of the analytical method requires comparison of the analytical parameter by means of both methods. Also mutual correlation of compared methods as well as recalculation of the parameter value which is measured by means of one method in terms of the value which corresponds to determination by means of another method, including pedotransfer functions are needed. Statistical distribution of the SOC determination according to the Ťurin method in Nikitin modification (TN) and by means of the analyser Euro 3000 (EA) in the observed set of samples is shown in the Table 2.

The data in the Table 2 clearly proves that the difference between average values of the SOC determined by means of the EA and TN methods is lower than 7%, which is an acceptable error for this type of measurements. The difference in both compared methods is changed by the SOC content. A significantly lower difference is for soil samples with the SOC content up to 3% and in the case of the higher SOC content, the difference between both compared methods is higher. The average value of the SOC of the analysed set determined by means of the EA method is slightly higher in comparison to the average value of the SOC determined by means of the TN method (Table 2) and it is consistent with the literature-related data [12, 9, 7, 8). Determination of the SOC by oxidation with strong oxidiser in the case of a higher content of organic carbon in soil samples will not result in determination of the whole organic carbon [6]. In accordance with the literature-related data [6], our results also confirm the fact that in the case of a higher content of the SOC, the TN method underestimated real values of organic carbon in soil samples.

TABLE 2. BASIC STATISTICAL PARAMETERS OF BOTH METHODS (TN, EA) OF SOC DETERMINATION

	SOC (%)	
	TN	EA
arithmetic average	4.017	4.280
minimum	1.040	1.050
maximum	17.100	17.400
standard deviation	3.783	4.023

Results of regression analysis of the compared methods are found in the Table 3. Pedotransfer function for recalculation of the SOC using the EA to TN value (PTF TN):

$$\mathrm{POC}\ \mathbf{(TN) = 0.00965839 + 0.936203 * POC\ (EA)} \tag{1}$$

Pedotransfer function for recalculation of the SOC using the TN to EA value (PTF EA):

$$\mathrm{POC}\ \mathbf{(EA) = 0.0274721 + 1.05874 * POC(TN)} \tag{2}$$

On the basis of the ANOVA analysis results for pedotransfer functions PTF TN and PTF EA, it may be concluded that between PTF functions values and analytically determined values there are not significantly statistical differences (Fig. 1, 2). For this reason PTF functions may be used for the purpose of recalculation of the SOC values determined by means of the method TN on the basis of the values determined by means of the method EA. The regression analysis demonstrated the possibility of recalculation of the SOC analytical data in existing databases according to different methods with PTF functions with a very high degree of agreement. The data in the Table 3 clearly proves that the analytical value of the SOC determined by means of the TN, the related EA method and predicted value in soil samples with the SOC content up to 3% is almost identical. On the basis of the obtained results, it may be concluded that in soil samples with the SOC content up to 3% it is not necessary to recalculate analytical data when changing the analytical method of the SOC determination.

TABLE 3. ANOVA ANALYSIS OF PTF FUNCTIONS

	PTF TN (1)					PTF EA (2)				
	Sum of Squares	Df	Mean Square	F-Ratio	P-Value	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	1106.71	1	1106.71	8665.93	0.0000	1251.56	1	1251.56	8665.93	0,0000
Residual	9.83355	77	0.127708			11.1206	77	0.144424		
Total(Corr.)	1116.55	78				1262.68	78			
Correlation Coefficient	0.995					0.996				
R2	99.119 %					99.113 %				
Mean absolute error	0.2323					0.2555				

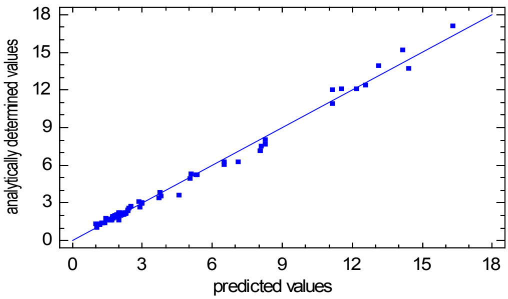

Fig. 1. PTF TN – Predicted values with PFT TN in the context with analytical SOC values (TN) in %.

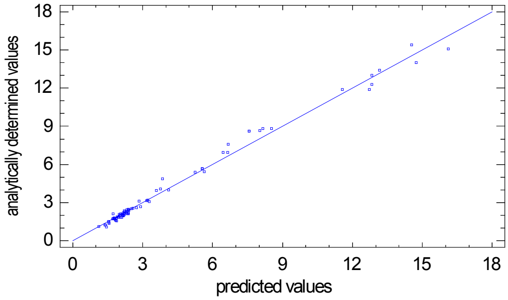

Fig. 2 PTF EA – Predicted values with PFT EA in the context with analytical SOC values (EA) in %.

Verification

Verification of PTF equations was carried out on the set of 17 samples of all studied localities sampled in 2012, which were not included into the pedotransfer analysis. Comparison of the analytically determined SOC and the SOC calculated with PTF as well as deviations of predicted and analytically determined values are found in the Table 4. Given the data shown in the Table 4 and Figure 3, it is clear that the highest differences in the SOC determination by means of the TN and EA methods have been found on soil samples of grassland on Leptic Umbrisol, Cambic Rendzic Leptosol, Molic Rendzic Leptosol , Umbric Andosol and Haplic Cambisol on acid parent materials (locality 11–13 and 16–17, Table 1) with the SOC values higher than 6%. On all these soil types on grassland, organic carbon concentration may reach 15–20% [4]. On these localities values determined by means of the EA were higher in comparison with the TN method. In soil samples with the SOC values up to 3%, differences between the analytical TN and EA methods are minimal and both of these methods may be used for the purpose of evaluation of trends in the SOC monitoring without losing previous time series.

TABLE 4. SOC VALUES (%) DETERMINED ANALYTICALLY (TN, EA METHODS), CALCULATED WITH PTF EQUATIONS AND BASIC STATISTICAL CHARACTERISTICS.

	SOC (TN)	SOC (EA)	PTF TN	PTF EA	R1	R2
Arithmetic average	5.218	5.581	5.230	5.550	-0.029	0.017
Minimum	0.810	0.910	0.860	0.880	-0.805	-0.442
Maximum	16.200	16.900	15.830	17.180	0.462	0.723
Standard deviation	4.455	4.790	4.480	4.720	0.289	0.265

R1 = differences between PTF TN value and analytically determined; SOC values SOC(TN)
R2 = differences between PTF EA value and analytically determined; SOC values SOC (EA).

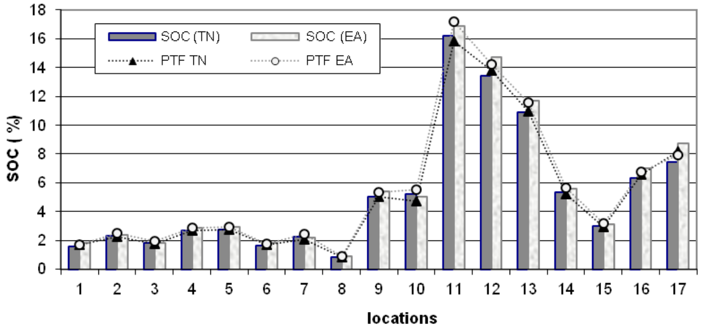

Fig. 3. Analytically determined SOC (TN) and (EA) in context with values calculated with PTF functions.

The SOC content up to 3% in the vast majority of arable soils of Slovakia may be found. However, our results show that in the case of the higher SOC content, which may be found mainly on grassland and alpine soils, it is necessary, when the analytical method is changed, to use PTF function (recalculation from the original method on the new one with the original data) in tracking trends, which reduces differences and allows to use the all time series monitoring data. In the case of higher organic carbon content in soils, without recalculation and PTF functions, it is impossible to statistically and significantly evaluate time changes of this parameter.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0243–11 and APVV-14–0087.

REFERENCES

[1] Barančíková G., Bezák P., Dodok R., Chlpík, J., Kobza J., Makovníková J., Píš V.: METHODS OF determining indicators of agrochemical soil properties. [In:] Hrivňáková, K., Makovníková, J. (Eds.): Integrated Procedures of Soil Analyses. VUPOP, Bratislava, 136, 2011.

[2] Commission of the European Communities: Proposal for a Directive of the European parliament and of the council establishing a framework for the protection of soil amending Directive 2004/35/EC, Brussels, 2006.

[3] Fiala K., Barančíková G., Bredková V., Búrik V., Houšková B., Chomaničová A., Kobza J., Litavec T., Makovníková J., Matúšková L., Pechová B., Váradiová D.: Partial Monitoring System – Soil. Relevant Methods. VUPOP, Bratislava,135,1999.

[4] Hansen H.C.B., Kobza J., Schmidt R., Szákal P., Borgaard O.K., Holm P.E., Kanianska R., Bognarova S., Makovníková J., Matúšková L, Mičuda R., Styk J.: Environmental Soil Chemistry. Univerzita Mateja Bela, Banská Bystrica, 2001.

[5] Kobza J., Barančíková G., Čumová L., Dodok R., Hrivňáková K., Makovníková J., Náčiniaková-Bezáková Z., Pálka B., Pavlenda P., Schlosserová J., Širáň M., Tóthová G.: Soil Monitoring of the Slovak Republic. Actual state and development of monitoring soil properties as the basis for their protection and land use (2007–2012). VUPOP, Bratislava. 251, 2014.

[6] Kononova M.M.: Soil Organic Matter. Izdatelstovo Akademiji Nauk, Moskva, 312, 1963.

[7] Lettens S., De Vos B., Quataert P., Van Wesemael B., Muys B., Van Orshoven J.: Eur. J. Soil Sci., **58,** 1244, 2007.

[8] Makovníková J. Barančíková G**. :** Agrochemia, **8**, 27, 2004.

[9] Meersmans J., Van Wesemael B., Van Molle M.: Soil Use Management, **25,** 346, 2009.

[10] Meloun M., J. Militký J.: Statistical Analysis of Experimental Data. Academia, Praha, 953, 2004.

[11] Ogle M.S. , Paustian K. : Can. J. Soil Sci., **85,** 531, 2005

[12] Pansu M., Gautheyrou J. : Handbook of Soil Analysis. Springer-Verlag, Berlin, 993, 2006.

[13] Sotáková S.: Organic Matter and Soil Fertility. Príroda, Bratislava, 234, 1982.

[14] Stolbovoy V., Montanarella L. : Application of soil organic carbon status indicators for policy-decision making in the EU. [In:] Toth, G., Montanarella, L., RusCO, E. (eds.): Threats to Soil Quality in Europe. JRC Scientific and Technical Reports, 87, 2008.

[15] Walkley A., Black I.A. : Soil Sci., **37,** 29, 1934.

PORÓWNANIE DWÓCH METOD OZNACZANIA WĘGLA ORGANICZNEGO W GLEBACH

Celem pracy było porównanie wyników oznaczania węgla organicznego (SOC) w próbkach gleb dwoma metodami: spalania „na mokro“ (Tiurina) oraz spalania „na sucho“ w autoanalizatorzee CN. Analizowano 95 próbek gleb z 17 miejsc kompleksowego monitoringu gleb Słowacji, o zwawartości węgla organicznego od 1 do 15%. Analiza statystyczna wykazała, że różnice wyników oznaczania SOC dwoma metodami w próbkach o zawarości węgla do 3% nie były istotne statystycznie. Dla próbek o wyższej zawartości SOC, wyniki uzyskane metodą spalania „na sucho“ były istotnie wyższe niż uzyskane metodą Tiurina, dlatego do celów porównawczych zawartości SOC w tych glebach oznaczonych różnymi metodami należy stosować odpowiednie przeliczniki.