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Quantification of Organic Carbon in Soils of the Derived Savannah Using Four Different Methods

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ABSTRACT

Background and Objective: Several methods of organic carbon determination exist including wet combustion (Walkley Black, Tube digestion and potassium permanganate) and dry combustion (loss on ignition) method. Each method is characterized by both advantages and limitations. This study aimed at quantifying the amount of organic carbon in soil of the Derived Savannah. **Materials and Methods:** The organic carbon was determined using four different methods: Walkley Black Method, Tube Digestion Method, Loss on Ignition Method and Potassium Permanganate Method. The soil was sampled across two different locations with different properties. The soil samples were analyzed and the obtained results were subjected to descriptive statistics and linear regression using the JMP Statistical package. **Results:** Different amount of organic carbon was determined by the methods. The loss on ignition determined the highest amount of 9.96 g kg^{-1} while, 5.81 g kg^{-1} was determined using Walkley Black. The use of permanganate and tube digestion was observed to determine 4.34 g kg^{-1} and 2.18 g kg^{-1} organic carbon, respectively. The results of the regression coefficient were observed to be >0.6 with the loss on ignition having a very good fit with an r^2 value of 0.99. **Conclusion:** The high amount of organic carbon produced by the loss on ignition and potassium permanganate could encourage their use for soils of savannah in addition to the little or no waste generated by this method.

KEYWORDS

Organic carbon, dry combustion, wet combustion, Walkley Black, Tube Digestion Method, Derived Savannah

INTRODUCTION

Agricultural activities are a dominant feature of the Nigerian Savannah and the intensive cultivation of this land has increased the pressure on the productivity of the land[1]. This has resulted in a decrease in fertility and consequently soil organic carbon[2]. The campaign for food security in Nigeria cannot be achieved without an adequate understanding of the soil's capacity to sustain crop growth[3]. To ensure sustainable soil productivity, consolidation of the basic methodology of soil properties determination is necessary and especially soil organic carbon determination.

The determination of soil organic carbon is a necessary measure of soil property due to its effect on the soil's physical and chemical properties such as the supply of plant nutrients and improving moisture holding capacity of the soil[4]. Generally, soil organic carbon can be quantified using two basic methods,

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wet digestion and dry combustion methods. In wet digestion, the soil carbon is oxidized by permanganate and sulphuric acid, this method is also known as the Walkley Black Method[5,6]. However, several modifications to this method have been carried out and reported such as the application of external heat or change in acid[7-10].

On the other hand, the dry combustion method is based on the oxidation of SOC at high temperatures and the carbon dioxide that is produced is determined by either, (a) measuring the weight loss on ignition (LOI) and (b) using of automated instruments (organic carbon analyzers)[4,11].

Each method has its advantages and limitations and different relation with soil texture and mineralogy and the method efficiency also depends on the methods depends on the composition of the SOC[12,13]. Due to the absence of a standard method of soil organic carbon determination, comparing experimental results is thus difficult hence, creating problems in SOC evaluation. The differences in soil properties, management and wider existence of soil carbon ranges necessitate the need for high volume and a more accurate method of soil organic carbon determination. This research aims to (i) Quantify SOC using different methods and (ii) Determine the relationship between the different methods.

MATERIALS AND METHODS

Study Area: The research was carried out in the research and experimental laboratory of the Department of Soil Science, Faculty of Agriculture, Bayero University Kano, from February, 2021 to May, 2021.

Soil sampling and processing: Sampling was carried out across two different soil types in Nassarawa (Derived Savannah) at two different locations in the Derived Savannah, Duduguru (latitude 08°25' 11.4 and longitude 08°25'19.1 N) and Ombi found (latitude 08034'11.4 and longitude 08034'21.2 E). Sampling was carried out at an interval of 1 km at a depth of 0-20 cm. The samples were air-dried, passed through a 2 mm sieve and stored for onward analysis in the laboratory.

Laboratory analyses: Soil pH was measured in both water and KCl_2 at a soil: Water and soil KCl_2 ratio of 1:2.5 using a glass electrode pH meter. The particle size distribution, Total N, Available P and Cation exchange capacity (CEC) were determined following the procedures outlined by Mustapha *et al.*[2].

The organic carbon was determined using four different methods: Walkley Black Method, Tube Digestion Method, Loss on Ignition Method and Potassium Permanganate Method.

Walkley-Black (WB) Method: The organic carbon was determined following the procedures described by Mustapha *et al.*[8].

Tube digestion Method (modified walkley black method): The tube digestion method, was carried out using the same procedure as outlined above, however, external heat was applied to the mixture.

Loss on Ignition Method: The method of organic carbon was carried out following the procedures outlined by Mustapha[14]. The percentage of organic carbon was then calculated using the following relationship:

$$OM\ (\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

Based on the assumption that organic matter contains about 58% organic carbon, a correction factor of 1.72 was used to get the percentage of OC using the following relationship:

$$OC\ (\%) = \frac{OM\ (\%)}{1.72} \quad (2)$$

Potassium Permanganate Method: Organic carbon was determined according to the procedure of Weil *et al.*[9]. The concentration of Permanganate Oxidizable Carbon (POXC) was calculated using the following formula:

$$POXC\ (mg\ kg^{-1}) = 0.02\ mol\ L^{-1}\ (a + b \times Abs) \times (9000\ mg\ C\ mol^{-1}) \times \left(\frac{0.02\ L\ solution}{Wt}\right) \quad (3)$$

Where:

$0.02\ mol\ L^{-1}$ = Initial solution concentration
a = Intercept of the standard curve
b = Slope of the standard curve
Abs = Absorbance of unknown
9000 = Milligrams of carbon oxidized by 1 mole of MnO_4 changing from Mn^{7+}-Mn^{4+}
0.02 L = Volume of stock solution reacted
Wt = Weight of air-dried soil sample in kg

The value obtained was converted to % by dividing by 100.

Statistical analysis: Descriptive statistics was used to summarize the data for soil properties and amount of organic carbon obtained using the different methods at <5% level of significance. Linear regression was carried out to determine the relationship between the methods. The JMP Statistical package was used.

RESULTS

The results of the soil characterization were as shown in Table 1. The results showed wide variation in the difference in particle size distribution in both locations. The soil of Ombi were observed to have a high amount of sand fraction (81.08%) and was characterized as sandy loam while, the soil of Duduguru had low amounts of sand (47.48 %) and characterize as loam. Both locations we observed to be acidic with low amounts of nitrogen and CEC. Available P was low in Duduguru (5.69) and medium in Ombi (10.07 g kg^{-1}). The amount of organic carbon determined by the different methods was as shown in Table 2. Different

Table 1: Physical and chemical properties of the soils of Duduguru and Ombi

	Location			
	Ombi		Duduguru	
Property	Range	Mean	Range	Mean
Sand (%)	70.88-84.88	81.08	38.88-54.88	47.48
Silt (%)	0.56-16.56	4.96	20.56-46.56	30.16
Clay (%)	12.56-16.56	13.96	14.56-30.56	22.36
Soil textural class	**Sandy loam**		**Loam**	
pH_w	4.8-5.8	5.2	4.7-6.8	5.6
pH_{KCl}	4.4-5.2	4.8	4.0-5.2	4.8
EC(dS m^{-1})	0.01-0.15	0.03	0.01-0.11	0.03
Total nitrogen (mg kg^{-1})	0.03-0.07	0.05	0.04-0.28	0.11
Available P (mg kg^{-1})	2.72-38.50	10.07	2.41-12.58	5.69
Exchange acidity (cmol kg^{-1})	0.25	0.25	0.08-0.33	0.20
CEC (cmol kg^{-1})	7.48-19.47	12.71	4.33-18.12	8.71

Adapted and modified from Mustapha *et al.*[2]

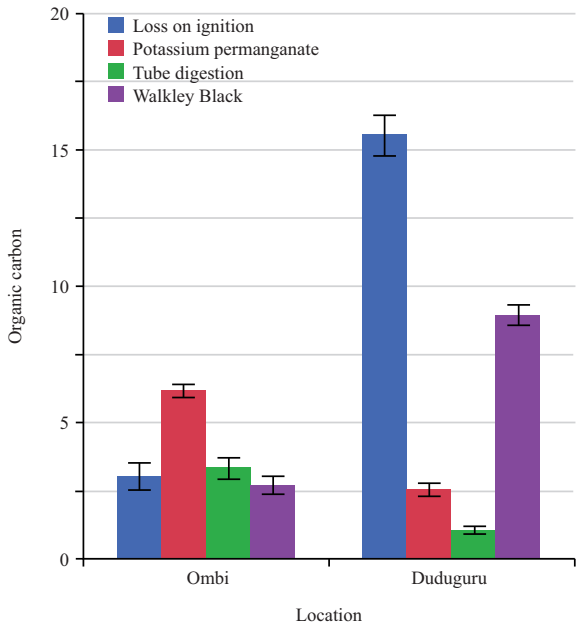

Fig. 1: Amount of OC determined by the different methods in each location
Bars are standard error

Table 2: Organic carbon determined by different methods

Methods	Minimum (g kg^{-1})	Maximum (g kg^{-1})	Mean (g kg^{-1})	Standard error	p-value
LOI	1.55	20.06	9.96	1.57	<0.0001
Potassium permanganate	1.79	7.31	4.34	0.44	<0.0001
Tube digestion	0.31	5.17	2.18	0.33	0.0002
Walkley Black	0.98	10.36	5.81	0.76	<0.0001

LOI: Loss on ignition

Table 3: Regression results showing the relationships between the different methods of determining soil organic carbon

Method				
x	y	a	b	R^2
Walkley Black	Loss on ignition	0.72	0.99	0.99
	Tube digestion	5.05	0.61	0.63
	Potassium permanganate	3.15	0.85	0.86

amounts of organic carbon were obtained by different methods. The highest amount of 9.96 g kg^{-1} was obtained with the use of LOI, followed by Walkley Black (5.81 g kg^{-1}). The tube digestion was observed to determine the lowest amount of carbon (2.18 g kg^{-1}). The amount of organic carbon determined in each location using different methods was shown in Fig. 1. In the soil of Ombi, the use of potassium permanganate determined the highest amount of OC (6.15 g kg^{-1}), while Walkley Black Method was observed to have to determine the lowest amount of 2.70 g kg^{-1}. The use of tube digestion and LOI determine 3.31 g kg^{-1} and 3.01 g kg^{-1}, respectively (Fig. 1). On the other hand, the use of the LOI was observed to determine the highest amount of OC for the soil of Duduguru followed by Walkley Black (8.93 g kg^{-1}). The lowest amount of carbon (1.05 g kg^{-1}) was obtained using the tube digestion method while, 2.54 g kg^{-1} of OC was determined with the use of potassium permanganate.

The results of the linear regression was shown in Table 3. The correlation coefficient between LOI and Walkley Black was the highest (R^2 = 0.99). The correlation coefficient was observed to be all methods and Walkley Black was observed to be 0.63 and 0.86 tube digestion and potassium permanganate, respectively.

DISCUSSION

Differences in soil properties across both location were observed. The soils of both location were observed to be dominated by sand which may be due to the granitic origin of these soils[15]. However in the soil of Duduguru, high amount of clay was observed which may be related to the highly weathered state of the soil[16]. Mustapha *et al*.[2] suggested that the use of acid-forming fertilizers could account for the observed acidity and the continuous soil cultivation and crop removal may have led to the low level of nutrients in these soils.

The quantification of OC using different methods could assist in making comparisons between different methods and selecting a method that extracts more OC in a given soil type. Wide variations in the amount determined were observed and generally, the amount of OC determined using the LOI was observed to extract the highest amount of OC among all the methods. The observed result was attributed to the oxidation of the different forms of carbon at their activation energies, thus resulting in a higher result compared to the other methods used[17]. The soil may also contain a high amounts of fulvic and humic acids, thus the high amount of OC obtained may be related to the degradation and decarboxylation reactions of these acids that occur at the high temperature used in this method[17]. The high amount may also be a result of over estimation due to the weight loss attributed to the volatilization of hygroscopic and structural water along with the weight of organic compound lost in the form has CO_{24}. The high yield of this method may prove as a more accurate measure of OC on soils of this area particularly for the soil of Duduguru as earlier reports by Wang *et al*.[8] showed an underestimation of OC with the use of Walkley Black. Similar high results with the use of LOI was reported by Mustapha[14] and Sharu *et al*.[15].

The use of potassium permanganate was observed to determine relatively low amount of carbon, though it determined the highest amount of OC in the soil of Ombi. The soil of Ombi could be rich in aromatic and phenolic compounds that have high reactivity with manganese, thus accounting for the results observed with potassium permanganate[18]. The amount of the OC may also be related to the multi-valence states and highly reactive forms of permanganate[8]. Similar high results with Permanganate were obtained by Mustapha *et al*.[9] however, the permanganate was acidified.

Generally, it was observed that the amount of OC determined by Walkley Black was relatively lower than all the methods used in the soil. The low amounts of OC determined may be related to the protection of the mineral fraction during the oxidation reaction with dichromate[12]. Similar poor results were obtained with the use of the tube digestion method and were attributed to non-target oxidation[5]. The high coefficient of correlation observed for LOI and potassium permanganate is an indication of their effectiveness in the determination of OC in comparison to Walkley Black[13].

CONCLUSION

Wide variations in the amount of OC determined by the different methods were observed. The amount of OC produced by the LOI was greater than all other methods in the soil of Duduguru, while, in the soil of Ombi, potassium permanganate was observed to produce a better result. Both methods have the potentials of replacing the use of the Walkley Black method on these soils especially has the volume of toxic waste generated is minimal.

SIGNIFICANCE STATEMENT

This study evaluated four different methods of organic carbon determination on the soils of the derived savannah. Variation in the amount of organic carbon determined by the different methods was observed, the use of loss on ignition and permanganate was observed to give better results in comparison to the other methods used. The use of these two methods (loss on ignition and permanganate) should be explored as alternatives to the conventional wet oxidation of dichromate, especially with the/little or no toxic waste produced.

REFERENCES

1. Voncir, N., S. Mustapha, A.A. Amba and T. Kparmwang, 2006. Inherent fertility status of alfisols, incepfisols and entisols in the gubi soil series, Bauchi, Bauchi State, Nigeria. J. Appl. Sci., 6: 2825-2828.
2. Mustapha, A.A., N. Abdu and M. Mafara, 2021. Fertility status of some selected soils in the Savannah Region of Northern Nigeria. Prod. Agric. Technol. J., 17: 91-97.
3. Mustapha, A.A., 2021. Status and distribution of micronutrients in selected soil orders of the Northern Savannah Region of Nigeria. J. Agric. Econ. Environ. Soc. Sci., 7: 189-201.
4. Ramamoorthi, V. and S. Meena, 2018. Quantification of soil organic carbon-comparison of wet oxidation and dry combustion methods. Int. J. Curr. Microbiol. Appl. Sci., 7: 146-154.
5. Roper, W.R., W.P. Robarge, D.L. Osmond and J.L. Heitman, 2019. Comparing four methods of measuring soil organic matter in North Carolina soils. Soil Sci. Soc. Am. J., 83: 466-474.
6. Gelman, F., R. Binstock and L. Halicz, 2012. Application of the Walkley-Black titration for the organic carbon quantification in organic rich sedimentary rocks. Fuel, 96: 608-610.
7. Angelova, V.R., V.I. Akova, N.S. Artinova and K.I. Ivanov, 2013. The effect of organic amendments on soil chemical characteristics. Bulg. J. Agric. Sci., 19: 958-971.
8. Wang, X., J. Wang and J. Zhang, 2012. Comparisons of three methods for organic and inorganic carbon in calcareous soils of Northwestern China. PLoS ONE, Vol. 7. 10.1371/journal.pone.0044334.
9. Mustapha, A.A., N. Abdu, E.Y. Oyinlola and A.A. Nuhu, 2023. Evaluating different methods of organic carbon estimation on Nigerian Savannah soils. J. Soil Sci. Plant Nutr., 23: 790-800.
10. Weil, R.R., K.R. Islam, M.A. Stine, J.B. Gruver and S.E. Samson-Liebig, 2003. Estimating active carbon for soil quality assessment: A simplified method for laboratory and field use. Am. J. Altern. Agric., 18: 3-17.
11. Fernandes, R.B.A., I.A. de Carvalho Junior, E.S.R. Junior and E. de Sá Mendonça, 2015. Comparison of different methods for the determination of total organic carbon and humic substances in Brazilian soils. Rev. Ceres, 62: 496-501.
12. Conyers, M.K., G.J. Poile, A.A. Oates, D. Waters and K.Y. Chan, 2011. Comparison of three carbon determination methods on naturally occurring substrates and the implication for the quantification of 'soil carbon'. Soil Res., 49: 27-33.
13. Sato, J.H., C.C. de Figueiredo, R.L. Marchao, B.E. Madari, L.E.C. Benedito, J.G. Busato and D.M. de Souza, 2014. Methods of soil organic carbon determination in Brazilian savannah soils. Sci. Agric., 71: 302-308.
14. Mustapha, A.A., 2020. Comparison of different methods for the assessment of soil organic carbon in Northern Guinea Savanna Zone of Nigeria. J. Sustainable Agric. Environ., 18: 36-41.
15. Sharu, M.B., M. Yakubu, S.S. Noma and A.I. Tsafe, 2013. Characterization and classification of soils on an agricultural landscape in Dingyadi District, Sokoto State, Nigeria. Niger. J. Basic Appl. Sci., 21: 137-147.
16. Kome, G.K., R.K. Enang, F.O. Tabi and B.P.K. Yerima, 2019. Influence of clay minerals on some soil fertility attributes: A review. Open J. Soil Sci., 9: 155-188.
17. Ratnayake, R.R., G. Seneviratne and S.A. Kulasooriya, 2007. A modified method of weight loss on ignition to evaluate soil organic matter fractions. Int. J. Soil Sci., 2: 69-73.
18. Skjemstad, J.O., R.S. Swift and J.A. McGowan, 2006. Comparison of the particulate organic carbon and permanganate oxidation methods for estimating labile soil organic carbon. Soil Res., 44: 255-263.