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Investigation of Organic Carbon Using Rapid Dichromate Oxidation in Comparison with Dry Combustion Techniques among Three Groups of Two Different Sizes of Soils

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Abstract

The purpose of this research was to compare two methods for the determination of organic carbon (OC)-rapid dichromate oxidation technique and dry combustion technique, in three groups of two different sizes of agricultural soils in Thailand. Fifty four soils collected from 3 provinces-Nakorn Pathom, Samut Sonkhram, and Samut Sakhon were classified as followed; 26 clays, 12 clay loams, and 16 medium loams. The selected soil sizes were < 65 µm representing the metal-studied soil size and < 212 µm representing the general purpose studied soil size. The statistical comparison of OC between the two methods indicated that using rapid dichromate oxidation technique-(Walkley-Black method) gave significantly less amounts of OC in clay and clay loam for soil size < 65 µm, but for soil size < 212 µm, the amounts of OC in clay were significantly less than those obtained from dry combustion technique. This implied that the amounts of OC associated to the soil particle size differently. In this study, the smaller of the soil particles the more underestimation of the amounts of OC were obtained by using rapid dichromate oxidation techniques. Therefore, we introduce new correction factors for the rapid dichromate oxidation technique: 1.37, 1.37, and 1.46 for clay and clay loam of soil size < 65 µm and clay of soil size < 212 µm, respectively.

Keywords: organic carbon; walkley-black method; clay; clay loam; medium loam; dry combustion technique

1. Introduction

Organic carbon (OC) is an important parameter for measuring soil quality. The two international standard methods are wet and dry combustion techniques which provide highly accurate results. The rapid dichromate oxidation technique, the so-called Walkley-Black method (WB method) is more used, since it is an easy and fast procedure (Walkley and Black, 1934; Sims and Heckendorn, 1991; Tiessen and Moir, 1993; Nelson and Sommers, 1996; Faithfull, 2002). However, this technique does not result in complete oxidation of organic compounds in the soil, and the average recovery of this method was 76% (Walkley and Black, 1934 cited by Nelson and Sommers, 1996). So, Walkley and Black (1934), cited by Nelson and Sommers (1996), proposed 1.3 as a correction factor (CF) to normalize the number close to the real value. This CF has been widely used up until now for general soil that has no specific CF. Nevertheless, the average of CF might vary from 1.0-1.4 for different groups of soils at different locations (Nelson and Sommers, 1996). Since recoveries of OC of WB method were highly variable, the set of analysis to quantify CF of each group of soil is needed. In Thailand, there is no previous report on CF of any type of soil. Therefore, in this study, three groups of soils-clay, clay loam, and medium loam were selected and compared to be the first database. Two different sizes of soil, <65 µm representing the metal-studied soil size and <212 µm representing the general purpose studied soil size were also studied to find the common ground for using the same CF for the same soil if soils had different sizes.

2. Materials and Methods

2.1. Soil sampling and preparation

Fifty fours fruit agricultural soil samples, collected from three provinces, Nakorn Pathom, Samut Sakhon, and Samut Songkhram, were classified as clay, clay loam and medium loam. They were collected at 15 cm-depth and air dried in the laboratory. Each sample was sieved with 65 and 212 µm and kept in plastic bag for further analysis.

2.2. Soil characteristics

Soils were characterized for common chemical properties according to Sparks *et al* (1996).

2.3. Dry combustion technique

The dry combustion procedure was done by burning the sample at 1000 °C in a stream of purified O_2 gas. The produced CO_2 gas was analyzed in a

Table 1. Organic carbon obtained from two methods among three groups of soils at two different grain sizes

Soil Size	Group of soil	No. of soil samples	Organic Carbon (mg/g soil) Mean ± SD	
			WB method	Dry combustion
< 65 µm	Clay	26	14.26 ± 3.970	15.01 ± 3.985[a]*
	Clay loam	12	11.90 ± 4.343	12.49 ± 4.343[a]*
	Medium loam	16	15.69 ± 4.362	15.10 ± 3.877[a]
< 212 µm	Clay	26	14.12 ± 5.054	15.01 ± 4.216[x]*
	Clay loam	12	13.26 ± 5.097	13.51 ± 4.963[x]
	Medium loam	16	16.70 ± 4.657	16.84 ± 4.391[x]

Note: SD = standard deviation; [a or x] = the same letters indicating no difference among groups of soil (P>0.05); * = significant difference between two methods (P<0.05)

Total Organic Carbon Analyzer (TOC) Teckmar-Dohrmann Phoenix 8000. The weighed soil sample was delivered in a platinum boat and burnt at 1,000°C. Inorganic carbon (IC) was determined with acid dissolution technique according to Loeppert and Suarez (1996). Then, the total organic carbon (TOC) was obtained by subtracting inorganic carbon from total carbon (TC).

2.4. Walkley-Black method

The rapid tritimetric oxidation technique or Walkley-Black method (WB method) was used to obtain organic carbon (WB result) in this study (Nelson and Sommers, 1996). The principal of this method was oxidizing OC with the hot mixture of $K_2Cr_2O_7$ according to equation (1).

$$2Cr_2O_7^{2-} + 3C^0 + 16H^+ \Leftrightarrow 4Cr^{3+} + 3CO_2 + 8H_2O \quad (1)$$

After the reaction (1), the excess $Cr_2O_7^{2-}$ was titrated with $Fe(SO_4)_2 \cdot 7H_2O$, and the reduced $Cr_2O_7^{2-}$ during the reaction with soil was equivalent to the organic carbon present in the sample described in equation (2).

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \Leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (2)$$

The results were calculated according to the following formula equation (3), using a correction factor (f) = 1.30, or a more suitable value found experimentally.

$$\%Organic\ Carbon = \frac{(mL_{blank} - mL_{sample})(M_{Fe^{2+}})(0003)(100)}{dry\ wt. of\ soil, g} \times f \quad (3)$$

$M_{Fe^{2+}}$ = Concentration of Fe^{2+}, 0.5 N.
mL_{blank} = The volume of 0.5 N $FeSO_4$ from the titration with blank, mL.
mL_{sample} = The volume of 0.5 N $FeSO_4$ from the titration with sample, mL.

The new correction factor calculation was done by the equation (4).

$$new\ correction\ factor = \frac{\%TOC_d \times dry\ wt. of\ soil}{100 \times 0.003 \times M_{Fe^{2+}} \times (mL_{blank} - mL_{sample})} \quad (4)$$

% TOC_d = total organic carbon (%) analyzed by dry combustion technique after eliminating inorganic carbon.

2.5. Statistical analysis

Statistical comparison between organic carbon obtained from WB method and dry combustion technique was paired t-test at α=0.05.

3. Results and Discussion

3.1. Soil characteristics

Of the 54 fruit farming, 26 samples were classified as clay, 12 samples as clay loam and 16 samples as medium loam. Their colors were in yellow-red type (data not shown). Most of them had a pH in the range of 6.5-7.5. For soil taxonomy, 33 soils were Inceptisols, 3 soils were Alfisols, and 22 soils were Mollisols (Department of Environmental Quality Promotion, 2003).

3.2. Comparison of organic carbon levels between two methods

From Table 1, the statistical comparison of OC using dry combustion technique among three groups of soils showed no significant difference within the same soil size ($p>0.05$) but when comparing between different sizes for the same group of soil (Fig. 1), only the medium loam group showed significant difference ($p<0.05$). The average amount of OC of medium loam for soil <212 µm was significantly higher than the average amount of OC for soil <65 µm. As the organic substances serve as binding agents for the cohesion of clay particles, such as through H-bonding and coordination with polyvalent cations (Stevenson,

Table 2. Correction factors for organic carbon not recovered by the Walkley-Black method

Soil Size	Group of soil	No. of soil samples	Organic carbon recovery (%) Mean ± SD	Average Correction factor
< 65 μm	Clay	26	94.8 ± 4.84	1.37
	Clay loam	12	94.9 ± 4.74	1.37
	Medium loam	16	103.9 ± 9.61	1.26
< 212 μm	Clay	26	91.8 ± 13.55	1.46
	Clay loam	12	97.7 ± 6.99	1.34
	Medium loam	16	99.6 ± 12.04	1.32

1994), they help forming good aggregates in a wide range of soil types (Anderson *et al.*, 1981; Anderson and Paul, 1984; Laird *et al.*, 2001; Virto *et al.*, 2008), particularly those representatives of the Mollisols, Alfisols, Utisols, and Inceptisols (Stevenson, 1994). This would explain why the amount of OC was found more and making the difference in larger particles at different sizes, while in clay and clay loam, which were of smaller sizes, their OCs were found less making the comparison between OC of two sizes no difference.

The amounts of OC from WB method and dry combustion techniques are shown in Table 1. The statistical comparison of OC between two methods showed significantly different of clay and clay loam for soil size <65 μm and only clay for soil size <212 μm ($p<0.05$). The amounts of OC obtained by WB method were significantly smaller than by the combustion technique. This indicates that the amounts of easy oxidizable OC seemed to be less when the soils were smaller in size, since the average soil particles among three groups of soils were as follows clay < clay loam < medium loam. This is probably because the types of OC associated with the soil fractions differ (Virto *et al.*, 2008; Tiessen and Stewart, 1983). Since most of the OC is usually stored in the clay size fraction (Anderson, *et al.*, 1981; Tiessen and Stewart, 1983), more clay particles provide more chance to contain more stable OC, such as polysaccharides, and condensed aromatic rings. Therefore, it might be more difficult to oxidize more stable OC with WB method in which it usually recovered only easily oxidizable OC.

As a result, new correction factors were needed. They are 1.37 for both clay and clay loam of soil size <65 μm and 1.46 for clay of soil size <212 μm (Table 2). From this point of view, the WB method with recommended CF 1.3 is useful without any need of further adjustment for medium loam of soil size <65 μm and for clay loam and medium loam of soil size <212 μm, others would need new CF; otherwise, the amounts of organic carbon would be underestimated.

4. Conclusions

The WB method is a fast and easy procedure to determine soil organic carbon. However, there is an inherent error that needs correction to bring the results close to the real values. Furthermore, types of OC that associated to the soil of different sizes have an influence on the WB method as well. One sample that was easily oxidized would yield the OC value close to dry combustion technique, while another sample that was more difficult to be oxidized did not. For three groups of Thai soils, only medium

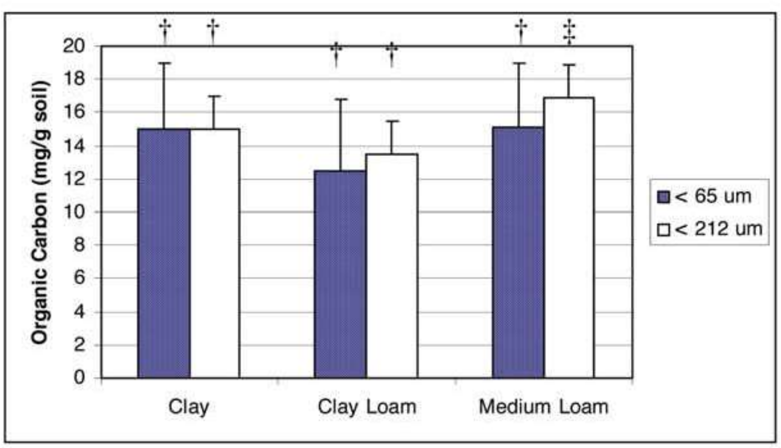

Figure 1. Organic carbons using dry combustion technique obtained from three groups of soil with different sizes: < 65 μm and < 212 μm (Bar chart = standard deviation; different cross symbols indicating significant difference of organic carbon between two sizes of soil ($p<0.05$)

loam could utilize the WB method and the recommended correction factor, 1.3 with no further adjustment for both sizes of soils, but for clay and clay loam, new correction factors would be needed especially for soil that was of smaller size; otherwise the underestimation of organic carbon would occur. Although the WB method could apply to medium loam directly, the amounts of OC obtained from two different sizes of soil were significantly different. So, the amounts of OC in each size of medium loam should be measured separately for further use.

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