研究簡報

Walkley-Black法分析土壤有機碳之回收率—以台灣非石灰質森林土壤為例

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摘 要

本研究分別以Walkley-Black法和元素分析儀分析562個台灣非石灰性森林土壤樣本的有機碳含量，以元素分析儀量測值為標準，探討Walkley-Black法氧化不同林型(針葉林、針闊葉混合林、暖溫帶闊葉林、針葉人工林、竹林一竹闊葉混合林、闊葉人工林、亞熱帶闊葉林)、化育層(A、B和C層)土壤有機碳的回收率(recovery rate)，與求其適用的校正值。結果Walkley-Black法測得、未經校正的有機碳濃度分布為0.06~36.4%，元素分析儀測值則為0.08~44.6%，回收率介於50.4至93.7%之間，平均為75.6%。森林土壤有機碳濃度之高低與Walkley-Black法之回收率無顯著相關。各林型皆以A層有較高的回收率，B和C層之間無顯著差異。雖然部分林型回收率有顯著差異，但諸林型之校正值頗為接近，其中A層校正值分布在1.19~1.27，B和C層在1.29~1.37，平均校正值分別為1.24和1.34。建議在較大範圍土壤有機碳估算時，仍可以用通用值1.30，但若欲更為精確估算台灣森林土壤有機碳含量時，A層可用1.24，B和C層可用1.34。

關鍵詞：Walkley-Black法、回收率、森林土壤、校正值。

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Research note

Recovery Rate of Organic Carbon by the Walkley-Black Procedure – Non-calcareous Taiwan Forest Soils as Examples

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【Summary】

Soil organic carbon (SOC) contents of 562 Taiwan non-calcareous forest soil samples were determined by the Walkley-Black (WB) method and an elemental analyzer. The data analyzed by the elemental analyzer were taken as the standard, to obtain the SOC recovery rate by the WB method in 7 forest types (coniferous forest, coniferous-broadleaf mixed forest, warm temperate broadleaf forest, coniferous plantation, bamboo/bamboo-broadleaf mixed forest, broadleaf plantation, and subtropical broadleaf forest) and their soil horizons (A, B, and C), in order to obtain suitable correction factors. SOC data of the WB method and the elemental analyzer were 0.06~36.4% and 0.08~44.6%, respectively. Recovery rates ranged 50.4~93.7% with an average of 75.6% for all samples. There was no significant correlation between SOC concentrations and WB recovery rates. All forest types had higher recovery rates in the A horizon than the B and C horizons, while no significant difference was found between the B and C horizons. Although recovery rates significantly differed among forest types, the correction factors were quite similar. Correction factors of the A horizon ranged 1.19~1.27, and those of the B and C horizons were 1.29~1.37, while averages were 1.24 and 1.34, respectively. It is suggested that a general value of 1.30 can be used to estimate the organic carbon content of a wide range of soils; however, for a more-accurate estimate of SOC contents in Taiwanese forests, the A horizon can use 1.24, and the B and C horizons can use 1.34.

Key words: Walkley-Black method, recovery rate, forest soil, correction factor.

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土壤有機碳(soil organic carbon; SOC)是土壤品質和生產力的重要指標，也是陸地生態系碳循環的重要的因子之一。Walkley-Black法(簡稱WB法)可以簡便、快速測定土壤有機碳含量，其利用重鉻酸鉀混合濃硫酸來氧化土壤的有機碳，以硫酸亞鐵銨滴定未消耗的重鉻酸鉀，估算土壤的有機碳濃度。但其主要限制為無法氧化有機碳組成中比較頑抗的成分，以致低估土壤有機碳含量，因而需校正值(correction factor; CF)矯正。WB法能氧化土壤中有機碳的百分比以有機碳回收率(recovery rate)表示，其倒數即為校正值。

近年，逐漸應用元素分析儀分析土壤有機碳含量，藉由高溫氧化土壤，產生的二氧化碳經氣體層析由熱傳導偵檢器(thermal conductivity detector, TDC)檢測(Nelson and Sommers 1996)，為目前公認能準確量測土壤總碳濃度(無機和有機碳)的方法之一，對非石灰性等不含無機碳的

土壤其測值十分接近土壤的總有機碳含量。因此，常以下列公式做為計算WB法氧化土壤有機碳回收率(WB recovery rate, WBR)的依據(Matus et al. 2009)，即WBR% = WBC_{NC}/EAC)×100，其中EAC為元素分析儀測得的總有機碳含量，WBC_{NC}為WB法測得、未經校正的有機碳含量。

Walkley and Black (1934)測定20個土壤有機碳回收率，平均為76%，提出校正值1.32，目前通用的校正值為1.30 (Nelson and Sommers 1996)。但，土壤有機碳回收率受土地利用、土壤類型、採樣深度和氣候等因子影響，不同地區的土壤各有其適用的校正值。例如，俄羅斯的黑鈣土，20 cm土層內，校正值與深度及耕作制度無明顯相關，皆適用1.63 (Miklailova et al. 2003)；喜馬拉雅山脈和印度中部的土壤有機碳回收率僅42和51%，校正值分別為2.40和1.95 (Krishan et al. 2009)；比利時北部溫帶低地森林適用校正值為1.77，農地適用1.51~1.59 (Lettens et al. 2007)；高溫多雨的熱帶昆士蘭，化育自花崗岩或變質岩的土壤適用1.24，而玄武岩、沖積土和河灘砂形成的土壤適用1.32 (Gillman et al. 1986)，但台灣並無相關的研究報告發表。如能建立台灣森林本土化的回收率，可降低土壤有機碳之分析費用，且能快速、較精確地收集國內土壤有機碳之資料。

本試驗以台灣非石灰性之林地土壤為樣本，涵蓋台灣海拔67~3306 m森林主要林型，樣本依林型類別分類，而林型分群主要參考垂直氣候帶區分植被的方式(Su 1984)，其中位處亞高山和冷溫帶的天然針葉林分別僅有6和4個樣點，樣本數較少故歸併為一類，以針葉林稱之；此外，人為干擾的人工林亦篩出分群，總計分為七類群，依其海拔由高至低分別為針葉林、針闊葉混合林、暖溫帶闊葉林、針葉人工林、竹林ー竹闊葉混合林、闊葉人工林、亞熱帶闊葉林(Table 1)。分別以WB法和元素分析儀(Elementar Vario EL III, Elementar Analysensysteme, Hanau, Germany)測定土壤的有機碳濃度(Nelson and Sommers 1996)，探討WB法氧化不同林地土壤有機碳的回收率，求出各林地適用的校正值，做為日後快速估算台灣森林土壤有機碳時的依據。

供試樣本於2010年2月2日至2011年8月11日期間採集，野外挖一土壤剖面，長、寬各1 m、深度為120 cm或達母岩層，依洗出層(A層)、洗入層(B層)和母質層(C層)分層收集，每分層分別收集1~2個樣本，總計141個土壤剖面，562個分層樣本(Table 1)。樣本攜回實驗室放入送風式烘箱以30~35℃乾燥後，磨碎、過2 mm的篩網，取已過篩的樣本，以瑪瑙研缽研磨、過80 mesh (< 180 μm)的篩網。為確認供試土壤為非石灰性土壤，取適量細磨的樣品，滴入數滴3.0 N鹽酸，無冒泡反應即不含碳酸鹽物質。分析數據使用SAS軟體統計。校正值CF以WB法測得的有機碳濃度(WBC_{NC})與元素分析儀測得的有機碳含量(EAC)的直線迴歸(無截距的迴歸式)方式求得(Meersmans et al. 2009)。

結果顯示EAC濃度分布為0.08~44.6%，WBC_{NC}含量為0.06~36.4% (Table 1)。個別林型A層有機碳(EAC)濃度為2.45~12.6%，B層為0.93~4.74%，C層為0.99~3.34%。經統計分析A層明顯較高，B和C層濃度比較低且彼此間無顯著差異($p > 0.05$)。各林型土壤有機碳平均濃度(A、B、C三化育層測值平均)以針葉林和針闊葉混合林比較高，竹林ー竹闊葉混合林、闊葉人工林和亞熱帶闊葉林比較低。碳濃度有隨海拔下降而漸減的趨勢。

各林型及土壤分層之土壤有機碳回收率介於50.4至93.7%之間，平均為75.6%。各林型皆以A層較高，其中只有竹林ー竹闊葉混合林化育層間差異較不明顯，其餘皆是A層顯著高於B和C層($p < 0.05$)。回收率較低的B和C層，因林型而互有高低，但差異皆不顯著($p > 0.05$)。因此，分別整併七林型的B和C層的測值(以B和C層表示)，列表如表2，進一步分析同類別化育層、林型間回收率之異同。

結果顯示A層土壤有機碳回收率在77.3~84.1%，其中以針葉林比較高，且與其他林型有顯著差異($p < 0.05$)，其他六類林型則差異不顯著(Table 2)。個別林型的校正值以針葉林略低為1.19，其他六林型校正值相近，範圍在1.24至1.27之間。分別針對A層以及B和C層兩

類群土壤之EAC和WBC測值繪製迴歸關係圖，結果皆具良好的線性相關性，整體A層的校正值為1.24 (Fig. 1A)。至於B和C層回收率則分布在71.2至76.2%，其中針葉林和暖溫帶闊葉林、針葉人工林有顯著差異($p < 0.05$)，其他林型則介於其間。各林型的校正值介於1.29至1.37之間，林型B和C層之平均校正值為1.34 (Fig. 1B)。

森林土壤的有機碳主要來自地被層累積之有機物。溫度為有機碳累積之重要因子，溫度愈高分解愈快，相對地，土壤積累的有機碳愈少。台灣因山高地陡，森林跨越多個氣候帶，溫度隨海拔上升而下降，山區森林地被層有機物聚積量之分布大致隨海拔上升而增加(Horng et al. 2003)，因此造成位處高海拔的林型累積了較高量的土壤有機碳。此外，干擾也會加速有機質的分解，頻繁地干擾(耕種)更加快土壤有機碳的耗損，但對其回收率並無顯著影響。Hussain and Olson (2000)研究不同耕種制度對有機碳回收率的影響，發現耕犁次數較多的農地有機碳明顯低於不耕犁的農地，但對有機碳回收率無明顯影響。我們雖然觀察到台灣人工林土壤有機碳濃度比相近海拔的林型略低，但其差異不顯著，可能是森林的干擾不似農地之頻繁所致。人工林的有機碳回收率與相近海拔的林型亦無顯著差異。

土壤有機碳濃度高低對其回收率影響不大，Amacher et al. (1986)研究美國路易斯安那州主要礦質土壤有機碳的回收率，指出回收率與總有機碳之間無明顯相關；De Vos et al. (2007)發現比利時溫帶低地森林(海拔3~118 m)的土壤有機碳回收率是隨著總有機碳含量增加而降低，但兩者相關性很低。台灣森林土壤有機碳回收率則是隨著有機碳濃度增加而微增，但兩者無顯著相關性($p > 0.05$)。台灣森林的A

Table 1. The soil organic carbon contents and recovery rates by the Walkley-Black method in different forest types

Forest type	No. of profiles	No. of samples	Elevation (m) Range	WBC_{NC} [1] (%)	EAC [2] (%)	WBR [3] (%)
Coniferous forest	10	36	2189-3306	0.50-36.4 [4]	0.68-44.6	66.7-93.7
				5.94 (8.27) [5]	7.30 (8.27)	79.5 (5.9)
Coniferous-broadleaf mixed forest	11	41	1290-2661	0.53-23.56	0.69-28.13	57.2-91.0
				5.21 (5.62)	6.69 (6.95)	75.5 (6.6)
Warm temperate broadleaf forest	53	214	503-1960	0.14-27.43	0.19-35.45	50.4-90.3
				3.64 (4.79)	4.69 (5.93)	74.4 (5.8)
Coniferous plantation	10	44	188-1945	0.27-18.22	0.44-22.19	61.9-83.8
				2.83 (3.56)	3.69 (4.41)	72.9 (2.9)
Bamboo/Bamboo-broadleaf mixed forest	9	37	732-1434	0.26-5.10	0.35- 6.45	70.6-81.7
				1.44 (1.16)	1.87 (1.45)	76.2 (3.0)
Broadleaf plantation	13	52	93-1101	0.06-3.23	0.08- 4.06	65.7-85.9
				1.02 (0.76)	1.33 (0.96)	76.1 (3.1)
Subtropical broadleaf forest.	35	138	67-666	0.16-6.48	0.19-7.43	56.5-90.4
				1.32 (1.14)	1.70 (1.41)	76.8 (5.0)

[1] The soil organic carbon determined by the Walkley-Black method, and no correction factor been used.
[2] The soil organic carbon determined by elemental analyzer.
[3] The soil organic carbon recovery rate by the Walkley-Black method, WBR% = WBC_{NC} / EAC.
[4] Range.
[5] Mean (standard deviation).

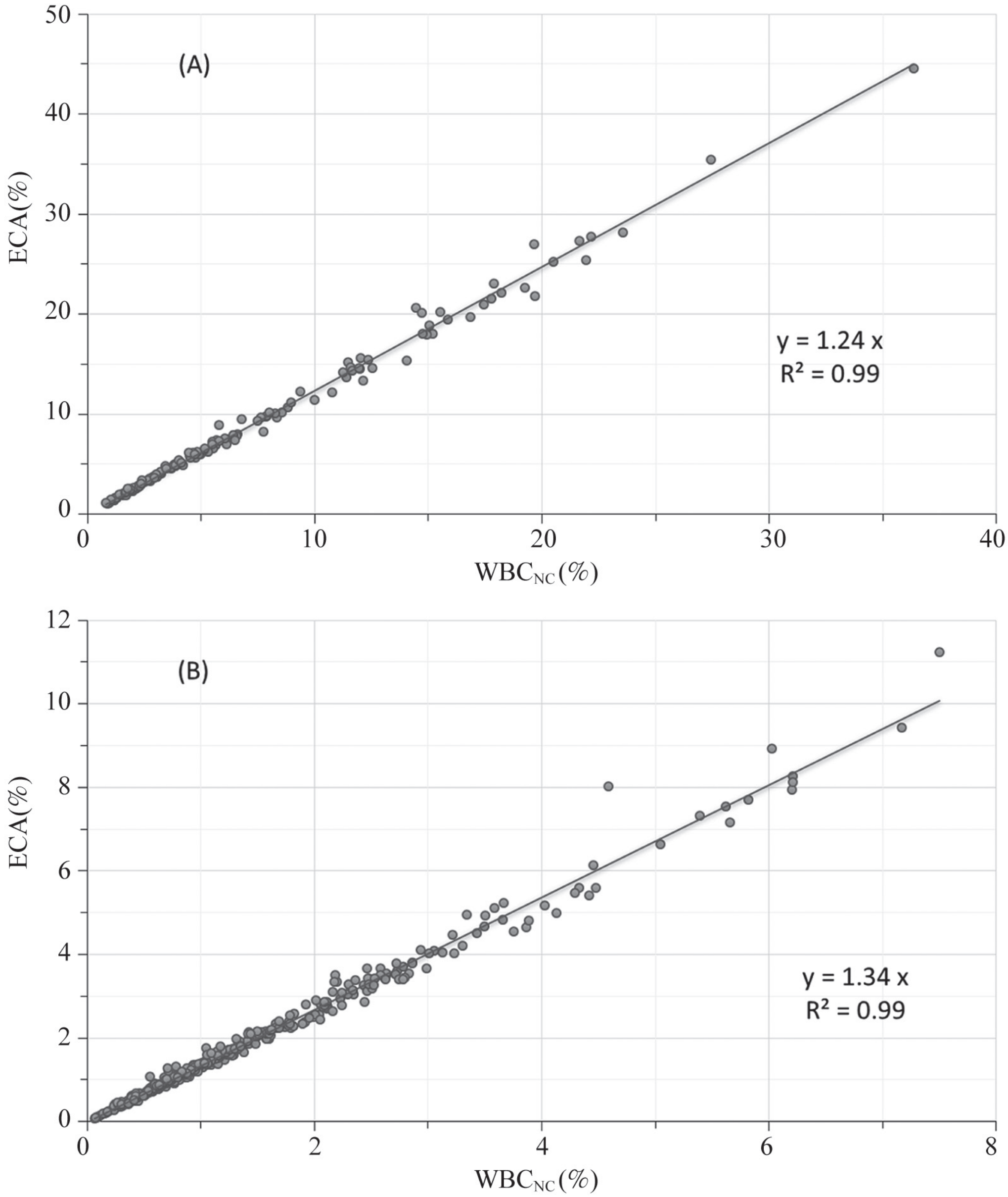

Fig. 1. Relationship between soil organic carbon contents of two soil horizons determined by the Walkley-Black method (WBC_{NC} %) and the elemental analyzer (EAC %). (A) A horizon (n = 156), and (B) B and C horizons (n = 406).

層不但是根系主要分布的土層，不定期還有颱風掠掃，補充地被層大量新鮮的枯枝落葉，位於上端的A層不缺新鮮有機碳來源，比其下方的B和C層累積更多容易分解的有機碳組成，此可能是台灣森林A層有機碳回收率普遍高於B和C層的主要原因之一。

綜觀各類林地的校正值，發現A層的校正值皆低於通用校正值1.30，B和C層多高於此值，顯然，以WB法、使用1.30時，會高估A層但會低估B和C層的土壤有機碳含量。A層估算

Table 2. Walkley-Black recovery rates (WBR%) and correction factors of different soil horizons in sampled forest types

Forest type	horizon	No. of samples	WBR (%)		EAC = $aWBC_{NC}$ [1)]	
			Range	Mean (stdev)	a[2)]	R^2 [3)]
Coniferous forest	A	14	77.6-93.7	84.1_A [4)]	1.19	0.99
Coniferous-broadleaf mixed forest	A	15	64.7-91.0	80.2_B	1.24	0.98
Warm temperate broadleaf forest	A	60	67.6-90.3	78.7_B	1.25	0.99
Coniferous plantation	A	12	70.6-83.8	77.3_B	1.25	0.99
Bamboo/Bamboo-broadleaf mixed forest	A	9	73.2-80.3	77.9_B	1.27	0.99
Broadleaf plantation	A	13	70.8-81.6	78.3_B	1.27	0.99
Subtropical broadleaf forest.	A	33	74.9-90.4	79.7_B	1.25	0.99
All Forest type	A	156	64.7-93.7	79.4	1.24	0.99
Coniferous forest	B&C	22	66.7-83.2	76.2_A	1.35	0.97
Coniferous-broadleaf mixed forest	B&C	26	57.2-80.6	73.5_{BC}	1.37	0.97
Warm temperate broadleaf forest	B&C	154	50.4-88.2	72.8_C	1.34	0.99
Coniferous plantation	B&C	32	61.9-80.4	71.2_C	1.37	0.99
Bamboo/Bamboo-broadleaf mixed forest	B&C	28	69.8-81.7	75.6_{AB}	1.29	0.99
Broadleaf plantation	B&C	39	70.8-81.6	75.3_{AB}	1.30	0.99
Subtropical broadleaf forest.	B&C	105	56.6-84.6	75.8_{AB}	1.31	0.99
All Forest type	B&C	406	50.4-88.2	74.1	1.34	0.99

1) The regression line between WBC_{NC} and EAC, where WBC_{NC} is the soil organic carbon determined by the Walkley-Black method. EAC is the soil organic carbon determined by elemental analyzer.
2) The slope of the regression line between WBC_{NC} and EAC, a: correction factor.
3) R^2: coefficient of determination.
4) Within a column in the same section, means with different letters are significantly different at $P = 0.05$ (Duncan's multiple range test).

誤差以針葉林略高，為8%；竹林—竹闊葉混合林和闊葉人工林二者較低，僅2%，其餘林型皆低於5%。相較之下，B和C層估算誤差比A層更低，皆低於5%，其中竹林—竹闊葉混合林、闊葉人工林和亞熱帶闊葉林等海拔較低的林地，其誤差甚至低於1%。

雖然，台灣森林土壤有機碳含量隨海拔上升而有增加的趨勢，但有機碳含量與其回收率無顯著相關。部分林型之土壤有機碳回收率有顯著差異，但整體而言，同一類別化育層的校正值卻頗接近，且與通用校正值1.30間之相對誤差百分比甚低，A層平均約5%，B和C層僅約3%。因此，建議在較大範圍土壤有機碳估算時，仍可以用通用值1.30，但若欲更為精確估算台灣森林土壤有機碳含量時，A層可用1.24，B和C層可用1.34。

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