COMPARISON OF THREE METHODS TO ESTIMATE ORGANIC CARBON IN ALLOPHANIC SOILS IN NEW ZEALAND

M Hasinur Rahman, Allister W Holmes, Markus Deurer, Steven J Saunders, Alistair Mowat and Brent E Clothier

The Carbon in Orchard Soils Team (COST), Plus Group Ltd., Horticulture Innovation Centre, Newnham Park, Te Puna, Tauranga, New Zealand E-mail: technical@plusgroup.co.nz

Abstract

Soil sequesters large amounts of carbon derived from organic and inorganic sources. Soil organic carbon (SOC) has to be measured periodically for the study of climate change. Many methods are used to estimate SOC and those methods are relatively time consuming and costly, with carbon in soil samples converted to carbon dioxide which is then measured directly or indirectly by different methods. Quantitative methods for the determination of SOC are based on titration or gravimetric, volumetric, spectrophotometric and chromatographic methods. Loss-on-ignition (LOI) has been considered as a rapid, inexpensive and convenient method for estimating SOC, which involves the dry combustion of samples at high temperature in a muffle furnace. The LECO Carbon Analyzer for SOC determination is capable of complete recovery and high precision, and is recommended primarily for total C analysis of soils. However, this method is costly and required a high level of user expertise to provide consistent performance. The objective of this study was to establish a NZ kiwifruit-specific regression equation to estimate SOC from LOI. We collected 121 allophanic soil samples from 0-100 cm depth from three regions of kiwifruit orchards in the Bay of Plenty area with organic, biological and integrated management systems. Soils were analysed using LOI to determine organic matter by combinations of three different ignition temperatures and four time durations. Results were compared with two other methods viz. wet acidified rapid dichromate oxidation, Walkley-Black method (organic carbon) and dry combustion technique, (LECO; total organic carbon) and a regression equation was established to estimate SOC in allophanic soil. A NZ kiwifruit-specific regression of SOC measured by LOI (A°C, a hours) versus LECO which was assumed here to have no error yields for the topsoil (0-50 cm) an R² of 0.822 and for the subsoil (50-100 cm) an R² of 0.45. The regression of SOC for 0-15 cm soils established by LOI (B°C, b hours) had an R² of 0.903. On the other hand, regressions established by LOI (300°C, 3h) for SOC of 15-30 cm and 30-90 cm of soils had R² of 0.777 and 0.748, respectively. This analysis shows that the LOI method is well suited as a cost-effective method for the analysis of SOC in NZ kiwifruit systems and other crops produced on allophanic soils, especially for topsoil.

Introduction

In soils there are three basic forms of carbon being elemental carbon, inorganic carbon, and organic carbon. Organic carbon or total organic carbon (TOC) is the amount of carbon bound in an organic compound. Soils contain a large variety of organic compounds ranging from simple sugars and carbohydrates to the more complex proteins, fats, waxes, and organic acids. Important characteristics of the organic compounds include their ability to form water-soluble and water insoluble complexes with metal ions and hydrous oxides; interact with clay minerals and bind particles together; absorb and desorb both naturally-occurring and anthropogenically-introduced organic compounds; absorb and release plant

nutrients; and hold water in the soil environment. As a result of these characteristics, the determination of total organic carbon is an essential part of any site characterization since its presence or absence can markedly influence how chemicals will react in the soil. Soil sequesters huge amounts of carbon derived from organic and inorganic sources i.e. soil organic carbon (SOC) has to be periodically measured not only for the study of climate change but also for the study of ecology. Carbon in soil samples is converted to carbon dioxide which is measured directly or indirectly by different methods. Many methods are used to estimate SOC and usually those methods are time consuming and costly. Loss-onignition (LOI) has been considered as a rapid, inexpensive and convenient method for estimating SOC, which involves dry combusting samples at high temperature in a muffle furnace. The purpose of this research is to answer the questions of (i) what is the most reliable, inexpensive and easy method for measuring SOC and (ii) what factors should be considered when selecting the method?

Materials and methods

We collected 121 allophanic soil (Vitrads/Vitricryands Andisol, USDA; Mollic Andosol, FAO; Ando Soil, Japanese system) formed predominantly from rhyolitic tephra between ~ 4000 and 40,000 years ago during the region's geographic history of periodic volcanic eruptions) samples from three regions (Katikati: 37°36S 175°56E; Tauranga: 37°43S 176°06E and Te Puke: 37°47S 176°23E) of kiwifruit orchards in the Bay of Plenty area of New Zealand with organic, biological and integrated management systems. The management practices of kiwifruit are stated elsewhere (Rahman et al., 2011). Soils were collected from 0-90 cm depth with three increments (viz. 0-15, 15-30 and 30-90 cm) by core method with opening a pit (Blake and Hartge, 1986). Soils were air dried and sieved through 2mm sieve. Processed soils were analysed for organic carbon by three recognised methods: wet chemistry-wet acidified rapid dichromate oxidation (Walkley & Black, 1934), dry chemistrydry combustion (TruSpec® CHN Determinators, LECO Corp., St. Joseph, MI, USA) and loss-on-ignition (Kalra, 1994). Because of the commercially sensitive nature of this work exact temperatures and durations are not given. Soils were analysed for LOI by factorial design with combinations of three different ignition temperatures (A, B and C °C) and four time durations (a, b, c and d hours). We placed oven dried (Gardner, 1986) soil samples in CEM disposable crucible and performed LOI in CEM Phoenix Microwave Furnace (Model #905410, CEM Corporation, Matthews, CA 28106, USA). Based on the results, a kiwifruitspecific regression equation was developed to estimate SOC from LOI with optimum ignition temperature and duration. All soil samples were stored in an electrical desiccator between being oven dried and LOI to reduce any chance of rehydration occurring.

Results and discussion

A NZ kiwifruit-specific regression of SOC measured by LOI (A $^{\circ}$ C, a hours) versus LECO which was assumed here to have no error yields for the topsoil (0-50 cm; SOC typically > 1%; SOC = -0.60833+0.57201*LOI) an R 2 of 0.882 (SD = 0.41 % SOC) and for the subsoil (50-100 cm; SOC typically < 1%; SOC = -0.38314+0.32517*LOI) an R 2 of 0.45 (SD = 0.17% SOC). The regression of SOC for 0-15 cm soils established by LOI (B $^{\circ}$ C, b hours) had an R 2 of 0.903 (Table 1); while regressions established by LOI (B $^{\circ}$ C, b hours)) for SOC of 15-30 cm and 30-90 cm of soils had R 2 of 0.777 and 0.748, respectively. Irrespective of soil depths, the relationship between SOC measured by LOI (B $^{\circ}$ C, b hours)) and LECO was established by a linear equation as: SOC = 0.5663*LOI-0.7589 with an R 2 of 0.922 which is highly significant at 1% level. Our results shows very poor relationship between LOI and LECO with higher temperatures and soil depths (Table 1), indicating LOI analysis on allophanic soils for subsoil or surface soils should involve lower temperatures. Furthermore,

we found the best correlation between LOI-LECO with the temperature-duration is $B^{\circ}C$ and "a" hours for optimum combination to estimate SOC from LOI for surface allophanic soils.

Table 1. Predicting SOC (y) from LOI (x) at various temperatures and durations.

Temperature	Duration		SOC(y) = mLOI + c					
$^{\mathrm{o}}\mathrm{C}$	hr	ı	m		С		r^2	
		WC*	DC**	WC	DC	WC	DC	
<u>0-15cm</u>								
A	a	0.744	0.494	1.620	0.191	0.805	0.822	
	b	0.890	0.595	-0.169	-1.035	0.654	0.676	
	c	0.885	0.586	-0.442	-1.120	0.590	0.591	
	d	0.868	0.573	-0.395	-1.110	0.593	0.598	
В	a	0.593	0.382	2.600	0.976	0.447	0.428	
	b	0.969	0.750	-2.536	-3.7045	0.704	0.903	
	c	0.925	0.615	-2.016	-2.233	0.721	0.738	
	d	0.945	0.618	-2.402	-2.356	0.744	0.734	
C	a	0.825	0.556	-1.695	-2.122	0.834	0.845	
	b	0.809	0.551	-2.442	-2.694	0.832	0.858	
	c	0.798	0.541	-2.347	-2.602	0.849	0.870	
	d	0.828	0.560	-2.875	-2.950	0.834	0.851	
<u>15-30cm</u>								
A	a	0.527	0.429	2.279	0.387	0.631	0.776	
	b	0.445	0.353	2.542	0.666	0.661	0.777	
	c	0.435	0.346	2.416	0.559	0.618	0.726	
	d	0.457	0.384	2.177	0.236	0.435	0.570	
В	a	0.223	0.217	3.645	1.272	0.107	0.189	
	b	0.248	0.205	3.351	1.288	0.173	0.219	
	c	0.262	0.235	3.203	0.988	0.204	0.305	
	d	0.278	0.239	3.032	0.913	0.241	0.330	
C	a	0.191	0.065	3.676	2.428	0.244	0.110	
	b	0.158	0.088	3.832	2.270	0.153	0.175	
	c	0.141	0.081	3.974	2.208	0.131	0.168	
	d	0.138	0.069	3.995	2.324	0.120	0.115	
<u>30-90cm</u>								
A	a	0.298	0.221	1.245	0.414	0.220	0.621	
	b	0.314	0.198	1.129	0.464	0.368	0.748	
	c	0.372	0.159	0.714	0.534	0.456	0.424	
	d	0.351	0.127	0.725	0.642	0.299	0.200	
В	a	0.115	0.026	1.784	1.102	0.055	0.014	
	b	0.152	0.000	1.565	1.229	0.105	0.000	
	c	0.028	-0.061	2.187	1.559	0.003	0.070	
	d	0.054	-0.052	2.031	1.524	0.010	0.051	
С	a	0.004	-0.041	2.318	1.479	0.000	0.043	
	b	0.016	-0.019	2.229	1.361	0.003	0.020	
	c	0.009	-0.028	2.272	1.424	0.001	0.041	
	d	-0.008	-0.045	2.399	1.555	0.000	0.063	

^{*}WC: Wet combustion- Walkley & Black, 1934; DC**: Dry combustion- LECO CHN auto analyser.

Conclusions

This analysis shows that the LOI method is well suited as a cost-effective method for the analysis of SOC in NZ kiwifruit systems. It is likely that LOI will also be suitable for other crops grown on allophanic soils, especially for samples obtained from the topsoil with higher accuracy than those from the subsoil. The LOI method may over-estimate the amount of carbon in Andisols because of its allophanic nature with high SOC which may adsorb water as a hygroscopic moisture in between oven drying and microwave furnace combustion occurring. Thus precautions should be taken to prevent the weight gain from hygroscopic moisture.

References

- Blake, GR and KH Hartge. 1986. Bulk density. In Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods, 2nd Edition. Ed. A Klute, 363-375. SSSA Book Series 5, Madison Wisconsin, USA.
- Gardner, WH. 1986. Water content. . In Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods, 2nd Edition. Ed. A Klute, 493-544. SSSA Book Series 5, Madison Wisconsin, USA.
- Walkley A and IA Black. 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Science 27: 29-38.
- Kalra, YP, and DG Maynard. 1994. Organic matter and organic carbon. In Methods manual for forest soil and plant analysis (Information Report NOR-X-319), 25-34. Edmonton, Alberta, Canada: Canadian Forest Service.
- Rahman MH, AW Holmes, AG M^cCurran and SJ Saunders. 2011. Impact of Management Systems on Soil Properties and Their Relationship to Kiwifruit Quality. Communications in Soil Science and Plant Analysis. 42(3): 332-357.