

Research Article

Application of Combustion Module Coupled with Cavity Ring-Down Spectroscopy for Simultaneous Measurement of SOC and $\delta^{13}\text{C}$ -SOC

Dan Liu,¹ Zhiguo Yu,² and Junjie Lin³ 

¹Department of Agricultural and Forestry Science and Technology, Chongqing Three Gorges Vocational College, Chongqing 404000, China

²School of Hydrology and Water Resources, Nanjing University of Information Science and Technology, Nanjing 210044, China

³Key Laboratory of Water Environment Evolution and Pollution Control in Three Gorges Reservoir, Chongqing Three Gorges University, Chongqing 404100, China

Correspondence should be addressed to Junjie Lin; ybu_lin@126.com

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Quantifying the decomposition of soil organic carbon (SOC) fractions under climate change is essential to predict carbon-climate feedbacks. The accuracy and utility of a combustion module coupled with cavity ring-down spectroscopy (CM-CRDS) system were assessed for simultaneously determining SOC and $\delta^{13}\text{C}$ -SOC. Using a range of standard materials as well as soil samples, we compared the results of the CM-CRDS system with those from other systems for determining C content and $\delta^{13}\text{C}$ value. The CM-CRDS system can determine a vast range of $\delta^{13}\text{C}$ values from -7.639% to -34.318% . The $\delta^{13}\text{C}$ values measured at C content > 0.2 mg C, corresponding to 1000 ppmv of CO_2 , were relatively stable. However, below a content of 0.2 mg C, the $\delta^{13}\text{C}$ values appeared unsteady and seemed to be affected by background signal. We found that, with the increase of C content, the recovery rates (RRs) for soil samples also increased. On the contrary, the RRs for inorganic materials were much lower than organic material and soil samples. Overall, the CM-CRDS system provides a valid alternative method to determine SOC and $\delta^{13}\text{C}$ -SOC for a sample simultaneously.

1. Introduction

Quantifying soil organic carbon (SOC) decomposition under climate change is essential to predict carbon-climate feedbacks and global C cycle [1, 2]. According to turnover times, SOC stocks can be divided into three fractions: annual cycling (aSOC), decadal cycling (dSOC), and millennial cycling, comprising of 0–5%, 60–85%, and 10–40% of total SOC stocks, respectively [3]. The approaches for investigating SOC fraction decomposition include improved measurement systems and labeling experiments using carbon isotope tracers (^{13}C or ^{14}C). Soils enriched with ^{14}C (“bomb carbon”) [4] or ^{13}C (natural ^{13}C tracer) [5] are used to investigate how climate change affects SOC decomposition in terrestrial ecosystems. Natural ^{13}C tracer studies take advantage

of the differences of $\delta^{13}\text{C}$ value between soil and plant, or soils had experienced a period of C_3 - C_4 (or vice versa) vegetation switch (e.g., continuous paddy ($\text{C}_3 \approx -26\%$) cropping of fields previously dominated by C input from C_4 vegetation $\approx -14\%$).

Previous studies have tested $\delta^{13}\text{C}$ -SOC by elemental analyzer coupled with isotope ratio mass spectrometry (IRMS) [6], gas chromatography (GC) coupled with IRMS [6], or nuclear magnetic resonance (NMR) spectrometry [7]. SOC is traditionally measured using either an elemental analyzer [8] or by the chromic acid titration method [9]. CM-CRDS system has been recently developed for isotope test in soil, plant, rock, and so forth. Onac et al. measured guano samples to explore guano-derived $\delta^{13}\text{C}$ -based paleohydroclimate record [10]. Li et al. analyzed leaf stable C isotope

TABLE 1: Site information.

Site	Location	MAT (°C)	MAP (mm)	Planted (years)	Vegetation	Soil type	Soil texture	C3 to C4 vegetation switch
Shenyang	42.7°N 125.1°E	5.2	1518	1961	<i>Zea mays</i> L.	Aquic brown soil	Sandy loam	15 years
Haerbin	45.6°N 126.6°E	3.1	530	1988	<i>Zea mays</i> L.	Terra nera	Sandy loam	23 years
Guigang	22.9°N 109.5°E	22.0	653	1956	<i>Saccharum officinarum</i> L.	Laterite	Clay loam	55 years

MAP: mean annual precipitation; MAT: mean annual temperature.

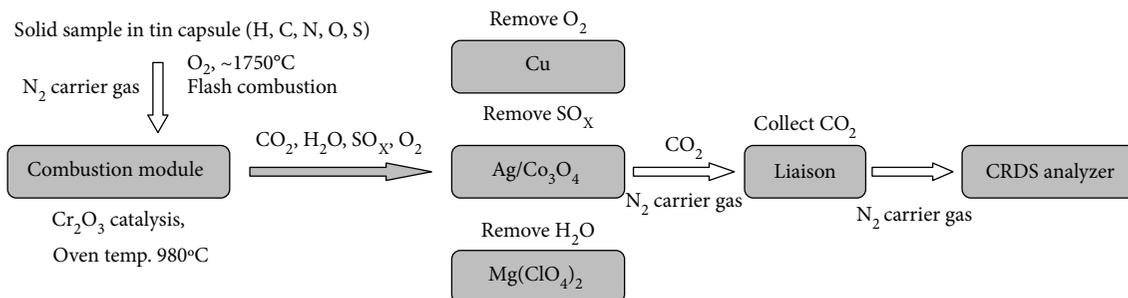


FIGURE 1: Schematic representation of the experimental setup for CM-CRDS [18].

composition by the CM-CRDS system with 0.2–0.3‰ precision [11]. Petrillo et al. measured the total C content and the $\delta^{13}\text{C}$ isotopic ratio of wood powder for decomposition of coarse woody debris about different elevation [12]. Qiu et al. used CM-CRDS to measure the $\delta^{13}\text{C}$ isotope in C_3 and C_4 plant for calculating plant water use efficiency [13]. Rossier et al. used CM-CRDS to measure the dried residue of wine to assess the production method of sparkling wine [14]. Burud et al. analyzed soil C content and $\delta^{13}\text{C}$ signature for calculating biochar mass percentage [15]. Shi et al. discussed the effect of doubled CO_2 concentration on the accumulation of photosynthate in *Lycium barbarum* by CM-CRDS [16]. Hayes et al. tested total C and $\delta^{13}\text{C}$ of mulch films to ensure the effect of weathering conditions on the physicochemical properties of biodegradable plastic mulches [17]. To date, few studies have reported the application of CM-CRDS system for simultaneous measurement of SOC and $\delta^{13}\text{C}$ -SOC in soil samples.

In this study, combustion module (CM) coupled with CRDS system was explored as an alternative method for making bulk measurements of SOC and $\delta^{13}\text{C}$ -SOC. CM-CRDS system provides a method that combines information about the quantity and isotopic signature of SOC for a sample in one measure. With this method all organic carbon in samples is converted into CO_2 by 1600–1800°C combustion, avoiding ^{12}C versus ^{13}C fractionation effects due to derivatization processes. We tested the CO_2 conversion efficiency of the combustion using different organic standards with different molecular structure and stability. The recovery rates for standard substances were also determined. Finally, the method was applied to natural samples for SOC and $\delta^{13}\text{C}$ -SOC, obtained with CM-CRDS system, and was compared with the results from other techniques.

2. Methods and Materials

2.1. Soil Sampling and Preparation. The surface soil samples (0–20 cm) that had experienced a period of C_3 - C_4 (or vice versa) vegetation switch were collected (Table 1). The samples were passed through a 2 mm sieve, thoroughly homogenized, and air-dried in the field. Visible roots and stones were carefully removed and milled for 5 min prior to the measure.

2.2. CM-CRDS System. A combustion module (CM) coupled to CRDS system (G2131-*i* Analyzer, Picarro Inc., USA) was used for SOC and $\delta^{13}\text{C}$ -SOC (Figure 1). The system was controlled by Picarro G2000 iCO_2 host software. Samples in tin capsules were loaded by an autosampler (Costech, USA) into the combustion module (980°C). The CO_2 collected by Picarro Liaison™ A0301 interface is inputted into CRDS for analysis.

Acetanilide ($\text{C}_8\text{H}_9\text{NO}$, C 71.09%, N 10.36%) and atropine ($\text{C}_{17}\text{H}_{23}\text{NO}_3$, C 70.56%, N 4.84%) were from Costech Analytical Technologies Inc., USA, and used as standards of carbon content. Glycine ($\text{C}_2\text{H}_5\text{NO}_2$, $\delta^{13}\text{C} = -33.3\text{‰}$) used as an isotopic reference material was purchased from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Calcium carbonate (CaCO_3 , $\geq 99.9\%$ p.a.) and sodium bicarbonate (NaHCO_3 , $\geq 99.5\%$ p.a.) were purchased from Kernel Chemical Reagents, China.

2.3. Comparison of Measurement Systems. Elemental analyser (Vario ELIII, Germany) was used to measure the SOC. Standard soil (carbon content = 2.01%) was procured from Starplex Scientific Inc. (Etobicoke, Canada). Acetanilide ($\text{C}_8\text{H}_9\text{NO}$, C 71.09%, N 10.36%) and atropine

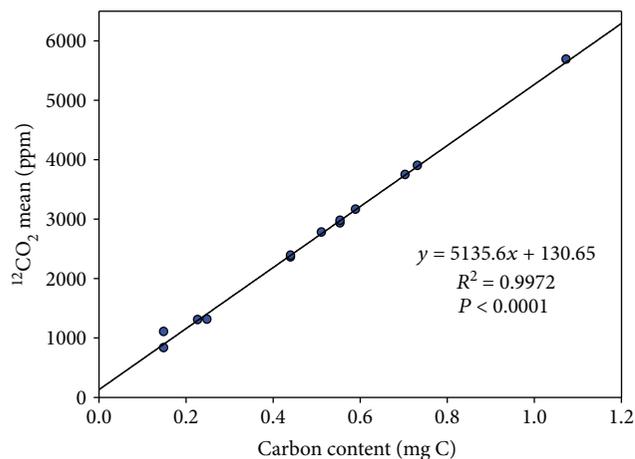


FIGURE 2: Standard curve for $^{12}\text{CO}_2$ concentration (ppm) versus C content (mg C).

($\text{C}_{17}\text{H}_{23}\text{NO}_3$, C 70.56%, N 4.84%) were obtained from Costech Analytical Technologies Inc. (Valencia, California, USA) and used as standards of carbon content.

The elemental analyser (Flash EA 1112) coupled online via a ConFlo III interface with a Deltaplus XP isotope ratio mass spectrometer (EA-IRMS, Thermo Finnigan, USA) was used to determine $\delta^{13}\text{C}$ -SOC. Urea ($\delta^{13}\text{C}$ vs_{PDB} = -45.380‰) and CO_2 ($\delta^{13}\text{C} = -29.523 \pm 0.181\text{‰}$) were used as working reference standards.

2.4. *Data Analysis.* Recovery rates (RRs) were determined as follows:

$$\text{RR} = \frac{C_i}{C_s} * 100\%, \quad (1)$$

where C_i is the measured content of a sample by CRDS and C_s is the concentration obtained with the comparison system (EA).

For isotopic measurements, the stable carbon isotope ratios are reported in delta notation expressed in per mil [19]:

$$\delta^{13}\text{C}_{\text{sample}} = \left(\frac{R_s}{R_{\text{st}}} - 1 \right) * 1000, \quad (2)$$

where R_s is the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample and R_{st} is the ratio of the international VPDB standard.

3. Results and Discussion

3.1. *Standard Curve.* We evaluated the linearity of the CM-CRDS method by plotting the measured $^{12}\text{CO}_2$ concentration against the carbon content (0.15–1.07 mg C) of acetanilide standard (Figure 2). We found a linearity between C content and $^{12}\text{CO}_2$ mean concentration with $R^2 = 0.9972$, $P < 0.001$. It is indicated that the CM-CRDS system has an acceptable CO_2 conversion efficiency for detecting the C content.

3.2. *Quantification of Soil Organic Carbon.* Four standards can be divided into three sorts, including organic (atropine),

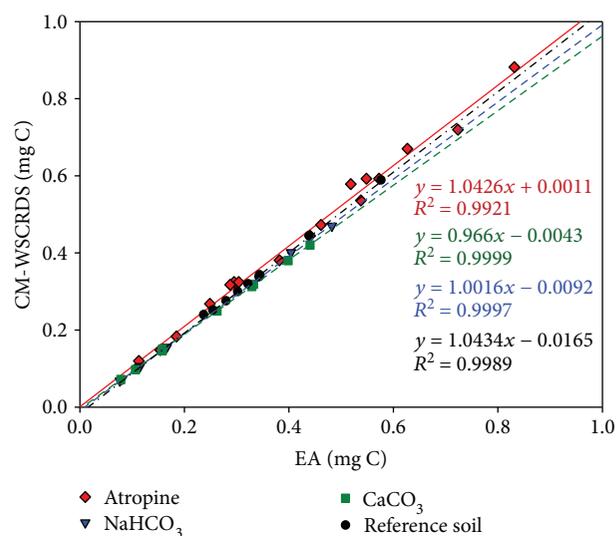


FIGURE 3: Correlation between contents determined by CM-CRDS and comparison system for standard materials and reference soil.

TABLE 2: Measured C content and recovery rates (RRs) of three standard materials and three soils determined by CM-CRDS and comparison system (EA).

Substance	EA (mg C)	CM-CRDS (mg C)	RR (%)
Atropine ($n = 4$)	0.2929	0.2938	100.31
NaHCO_3 ($n = 4$)	0.6226	0.6112	98.17
CaCO_3 ($n = 4$)	0.2973	0.2833	95.29
Soil-1 ($n = 5$)	1.7000	1.7618	103.63
Soil-2 ($n = 5$)	2.0779	2.1690	104.38
Soil-3 ($n = 5$)	2.2637	2.3763	104.97

inorganic (NaHCO_3 and CaCO_3), and soil reference. Aliquots were used for analysis by CM-CRDS and EA. We investigated the linearity of the CM-CRDS system by comparing the measured values of different contents from comparison method. For different standards, we found the same $^{12}\text{CO}_2$ peak areas at the equal C content with correlations constant of $R^2 > 0.99$ ($R^2 = 0.9921$ for atropine, $R^2 = 0.9997$ for NaHCO_3 , and $R^2 = 0.9999$ for CaCO_3). The slopes ranged from 0.966 to 1.0434 (Figure 3). The average recovery rates (RRs) for atropine, NaHCO_3 , and CaCO_3 were 100.31%, 98.17%, and 95.29%, respectively (Table 2). We also applied CM-CRDS to reference soil. For the comparison of SOC content measured with CM-CRDS with those obtained with the EA system, we found a correlation with $R^2 = 0.9989$ and a slope of 1.0434 (Figure 3). According to the values of R^2 and RRs from the three sorts of standards, we found that CM-CRDS system can give us satisfactory results as comparing method.

With the increase of C content, the higher RRs for soil samples were found (Table 2). On the contrary, the RRs for inorganic materials were much lower than organic material and soil samples. It indicated that EA system is limited in comparison with the CM-CRDS system for organic and soil samples.

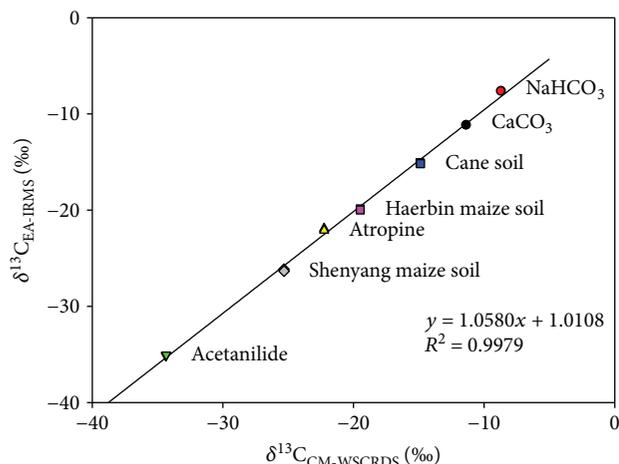


FIGURE 4: Correlation of $\delta^{13}\text{C}$ values measured by CM-CRDS ($n = 5$) and comparison system.

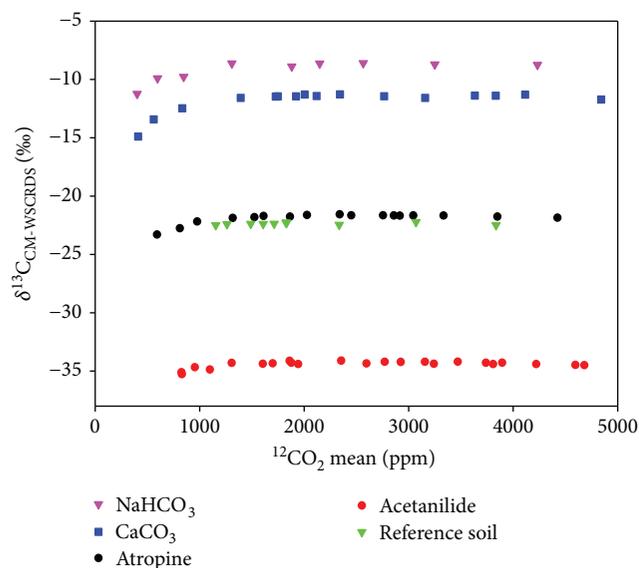


FIGURE 5: C content-dependent measurements of $\delta^{13}\text{C}$ values determined by the CM-CRDS.

3.3. Isotope Values of Standard Materials and Soil Samples.

The different standard materials were used to express that the CM-CRDS system can determine a vast range of $\delta^{13}\text{C}$ values (Figure 4). We found a linear regression with a slope of 1.0603 and a $R^2 = 0.9982$. The heaviest $\delta^{13}\text{C}$ value was determined for NaHCO_3 (-7.639‰) and the lightest for acetanilide (-34.318‰). Balslev-Clausen et al. found the similar degree of correlation when they compared the $\delta^{13}\text{C}$ values measured with CM-CRDS with values determined by a continuous flow- (CF-) IRMS system for rock samples [18].

We also found C content-dependent variations in the $\delta^{13}\text{C}$ values for all standards materials within a C content range of 0.2–1.1 mg C (Figure 5). Below a content of 0.2 mg C, the $\delta^{13}\text{C}$ values appeared unsteady and seemed to be affected by background signal. However, the $\delta^{13}\text{C}$ values

measured at contents >0.2 mg C, which corresponded to 1000 ppmv of CO_2 , were relatively stable. Moni and Rasse recently detected C content and $\delta^{13}\text{C}$ signature in vegetation samples by CM-CRDS [20]. However, ^{13}C -labeled CO_2 was used to simulate a leak from geologically stored CO_2 , which cannot represent the situation of samples in the natural ^{13}C abundance. Ignoring the molecular structure and complexity of a sample, the combustion module (CM) facilitates the conversion of hydrocarbons to CO_2 and water. Thus, heterogeneous soils can also be analyzed with this system. This verifies the isotope analysis of rock [18] and volatile liquid [21], geologically stored CO_2 [20], amino acids [22], and insects [23].

To summarize, even small changes in soil CO_2 released from SOC decomposition can significantly affect atmospheric CO_2 concentration and global C cycle. Thus, the interest in estimating the contribution of different fractions of SOC to soil C respired under climate change in the terrestrial ecosystem has increased in recent years. The CM-CRDS system can be used to determine SOC and $\delta^{13}\text{C}$ -SOC simultaneously. In our investigation, the CM-CRDS system was characterized by a high signal to noise and more accurate measurements. To ensure the accuracy for a wide range of CO_2 concentration and reduce transient concentration response, the instrument needs to be recalibrated, and the processing software should be upgraded. Compared with EA and EA/IRMS systems, the CM-CRDS system has an equal or superior reproducibility, memory, and drift.

Conflicts of Interest

The authors declare they have no competing financial interests.

Authors' Contributions

Dan Liu and Zhiguo Yu contributed equally to this work.

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