Article

Carbon Dynamics and Fertility in Biochar-Amended Soils with Excessive Compost Application

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Abstract: In Taiwan, farmers often apply excessive compost to ensure adequate crop yield in frequent tillage, highly weathered, and lower fertility soils. The potential of biochar (BC) to decrease soil C mineralization and improve soil nutrient availability in excessive compost application soil is promising, but under-examined. To test this, a 434-day incubation experiment of in vitro C mineralization kinetics was conducted. We added 0%, 0.5%, 1.0%, and 2.0% (*w/w*) woody BC composed of lead tree (*Leucaena leucocephala* (Lam.) de. Wit) to one Oxisol and two Inceptisols in Taiwan. In each treatment, 5% swine manure compost was added to serve as excessive application. The results indicated that soil type strongly influences the impact of BC addition on soil carbon mineralization potential. Respiration per unit of total organic carbon (total mineralization coefficient) of the three studied soils significantly decreased with increase in BC addition. Principal component analysis suggested that to retain more plant nutrients in addition to the effects of carbon sequestration, farmers could use locally produced biochars and composts in highly weathered and highly frequent tillage soil. Adding 0.5% woody BC to Taiwan rural soils should be reasonable and appropriate.

Keywords: biochar; soil carbon dynamics; soil fertility; excessive compost application; Ultisols

1. Introduction

Soil degradation due to erosion, salinization, depletion of soil organic matter (SOM), and nutrient imbalance is the most serious bio-physical constraint limiting agricultural productivity in many parts of the world [1]. Maintaining an appropriate level of SOM and ensuring the efficient biological cycling of nutrients are crucial to the success of soil management and agricultural productivity strategies [2,3], including the application of organic and inorganic fertilizers, combined with the knowledge of how to adapt these practices to local conditions, aiming to maximize the agronomic use efficiency of the applied nutrients and thus crop productivity [3]. In soils with low nutrient retention capacity, strong rains rapidly and easily leach available and mobile nutrients into the subsoil, where they are unavailable for most crops [4], rendering conventional fertilization highly inefficient [5]. SOM has been reduced in the arable lands of Taiwan over the last several decades due to highly frequent tillage, in association with high air temperature and rainfall; in addition, farmers often apply excess compost to ensure adequate crop yield.

Depending on the mineralization rate, organic fertilizers, such as compost, mulch, or manure, release nutrients in a gradual manner [6], and may therefore be more appropriate than inorganic fertilizers for nutrient retention under high-leaching conditions. Due to the relatively low levels of nutrients (10–20 g N/kg and less than 10 g P/kg) in compost, compared to a complete fertilizer, as well as the low plant availability of compost N and P, a large amount of compost is needed to meet the N and P crop requirements [7], and farmers often apply excess compost to ensure adequate crop yield, leading to excessive N and P loading into the environment. In the tropics, however, natural rapid mineralization of SOM is a limitation of the practical application of organic fertilizers; in addition to repeated application at high doses and the cost of application of organic materials, their rapid decomposition and

mineralization may significantly contribute to global warming [8–10]. Excessive manure application often causes heavy metal accumulation (Cu, Pb, Zn, etc.) in the soil, and the soluble fraction of these metals tends to increase due to desorption and remobilization of metals previously bound to the soil matrix, leading to enhanced crop uptake of heavy metals [11]. In acidic and highly-weathered tropical soils, the application of organic fertilizers and charcoal increases nutrient stocks in the rooting zone of crops, reduces nutrient leaching, and thus improves crop production [5]. Biochar could be a key input in raising and sustaining production and simultaneously reducing pollution and dependence on fertilizers, and could also improve soil moisture availability and sequester carbon [12]. Biochar (BC) studies have mainly focused on the effects of pure BC addition or artificial fertilizers; however, pure BC does not provide a high amount of nutrients in most cases [13]. Incorporation of BC-compost into poor soil is considered a promising approach to produce a substrate like *terra preta*; the study demonstrated a synergistic positive effect of compost and BC mixtures on soil organic matter content, nutrients levels, and water-storage capacity of sandy soil under field conditions [13]. BC either helped stabilize manure C, or the presence of manure reduced the effect of BC on the mineralization of soil organic carbon (SOC) [14]. Trupiano et al. [15] showed that both BC amendment (65 g/kg) and compost (50 g/kg) addition to a moderately subalkaline (pH 7.1) and clayey soil poor in nutrients had a positive effect on lettuce plant growth and physiology, and on soil chemical and microbiological characteristics; however, no positive synergic or summative effects exerted by compost and BC in combination were observed compared to compost treatment alone. BC, compost, and the BC-compost blend have fewer environmental impacts than mineral fertilizer from a systems perspective [16].

In Taiwan, annual precipitation is about 2500 mm (ranging from 1500 mm to 4500 mm) and annual mean air temperature is about 23 °C (28~29 °C in summer, 16–19 °C in winter). Higher precipitation always results in enormous soil erosion and nutrient leaching, and warm temperatures cause rapid decomposition of soil organic matter. In addition, intensive and highly frequent tillage has resulted in obvious decrease of soil organic matter. These are major setbacks to Taiwan's agricultural soils. Harris et al. [17] suggested that proper soil organic carbon (SOC) content should be 4% to 6%. Wang et al. [18] indicated that the addition of 37 tons/ha organic fertilizer (carbon content was 58%) per year in rural Taiwan is necessary, and soil organic carbon can be maintained within an appropriate range. This is equivalent to 2% compost in general rural soil, considering 1800 Mg of soil per hectare (soil bulk density equal to 1.2 Mg/m and an arable soil layer of 15 cm). The carbon content of swine manure compost in this study is only 23.3%, much lower than the 58% mentioned above (Table 1). This suggests that [18] farmers should add at least 5% compost/ha/year to maintain appropriate soil organic carbon content. The 5% addition rate means adding 90 tons/ha compost to soil, as well as a large amount of 1800 kg N/ha and 900 kg P/ha to the soil. Taking into consideration economic viability, the doses of manure compost in Taiwan are recommended as 1% to 2%; however, some farmers apply more than 2% to 5% in intensive cultivation periods for short-term leafy crops, in an effort to add more N. However, in excessive compost application soils, little is known about the impact of BC application rates on the carbon mineralization and soil fertility of mixed-soils (BC, compost, and soil) in highly frequent tillage soil systems. The in vitro C mineralization kinetics of various BC addition rates in three selected soils were examined in this study. We hypothesized that the addition of BC may stabilize compost organic matter, diminish mixed-soil C mineralization, and improve soil nutrient status. Farmers can gradually reduce the addition of compost over the next few years by adding biochar to maintain appropriate SOC, reduce N, and prevent loss of nutrients. The aims of our research were: (1) to quantify the effects of woody BC additions on C mineralization and soil fertility, and (2) to evaluate the sustainability of woody BC additions in terms of maintaining high SOM content and nutrient availability.

Table 1. Characteristics of biochar, compost, and three studied soils.

Characteristics	Biochar	Compost	Pc Soil	Eh Soil	An Soil
	(BC)		(SAO)	(MAI)	(SAI)
pH	9.9 ¹	8.41 ¹	6.1/5.0 ³	7.5/7.2 ³	6.5/6.2 ³
EC (dS/m)	0.77 ¹ /1.36 ²	3.79 ¹	0.45	2.21	0.81
Sand (%)			11	24	33
Silt (%)			30	36	33
Clay (%)			59	39	34
Soil Texture			Clay	Clay loam	Clay loam
Total C (%)	82.5	23.3	2.03	1.11 (0.81) ⁴	0.94
Total N (g/kg)	6.99	22.6	2.71	2.32	1.58
Total P (g/kg)	0.55	10.2	1.16	0.98	0.77
Ex. K (cmol(+)/kg soil)	1.91	6.43	0.32	0.29	0.21
Ex. Na (cmol(+)/kg soil)	1.26	1.09	0.31	0.26	0.37
Ex. Ca (cmol(+)/kg soil)	3.62	2.70	4.85	2.94	2.24
Ex. Mg (cmol(+)/kg soil)	0.40	2.72	0.64	0.80	0.36
CEC (cmol(+)/kg soil)	5.20	19.7	8.58	11.5	14.2
BS (%)	100	69	71	37	22
M3-P (mg/kg)	96.6	6874	163	236	94.0
M3-K (mg/kg)	616	8911	68.4	108	94.1
M3-Ca (g/kg)	4.09	14.5	2.03	8.22	2.99
M3-Mg (mg/kg)	278	3972	143	344	401
M3-Fe (mg/kg)	65.5	396	524	589	1199
M3-Mn (mg/kg)	20.9	188	29.0	213	185
M3-Cu (mg/kg)	0.02	6.22	9.77	9.95	3.17
M3-Pb (mg/kg)	ND ⁵	1.23	10.8	11.7	1.54
M3-Zn (mg/kg)	0.35	62.4	20.4	7.98	5.28

¹ The pH and electrical conductivity (EC) of biochar and compost were measured using 1:5 solid: solution ratio after shaking for 30 min in deionized water; ² Biochar EC was measured after shaking biochar-water mixtures (1:5 solid: solution ratio) for 24 h; ³ Soil pH was determined in soil-to-deionized water ratio of 1:1 (g mL⁻¹) and in soil-to-1N KCl ratio of 1:1 (g mL⁻¹); ⁴ carbonate content; ⁵ ND = not detected.

2. Materials and Methods

2.1. Soil Characterization

Three representative rural soils derived from different parent material in Taiwan were selected for the incubation experiment. The Pingchen (Pc) soil series is a relict tertiary Oxisol (slightly acidic Oxisol, SAO) in Northern Taiwan [19]. The Erhlin (Eh) soil series is an Inceptisol (mildly alkaline Inceptisol, MAI) developed from calcareous slate old alluvial parent material in Central Taiwan. The Annei (An) soil series is also an Inceptisol (slightly acid Inceptisol, SAI) developed from calcareous sandstone-shale new alluvial parent material in Southern Taiwan. Rice is the commonly grown crop in the sampled fields. Soil samples were collected in spring 2011 from the upper layers (0–15 cm) of three fields in Taiwan. Field moist soil samples were air-dried at room temperature (25–28 °C), gently crushed and passed through a 2-mm sieve, and then stored at room temperature for physiochemical analysis. The physical and chemical characteristics of the top soils (15 cm depth) are presented in Table 1.

Soil pH was determined in a soil-to-deionized water ratio of 1:1 (g/mL) and in soil-to-1 N KCl ratio of 1:1 (g/mL) [20], and electrical conductivity (EC) was determined by saturation extract of the soil sample [21]. Soil particle size was determined using the pipette method [22]. Soil total C (TC) content was determined by dry combustion [23], using an O.I. Analytical Solid Total Organic Carbon (TOC) (O.I. Corporation/Xylem, Inc., College Station, TX, USA). Soil TC was assumed to be organic in nature because the low or neutral soil pH precludes carbonates. Soil total nitrogen (TN) content was extracted by digesting a 1.0 g dried and powdered sample using concentrated H₂SO₄ in a Kjeldahl flask using K₂SO₄, CuSO₄, and Se powder as catalysts. TN concentration was determined via O.I. Analytical Aurora Model 1030W (O.I. Corporation/Xylem, Inc., College Station, TX, USA); content of soil total phosphorus (TP) in the digested solution was determined with inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer, Inc., Optima 2100DV, Waltham, MA,

USA). The exchangeable bases (Ex-K, Na, Ca, and Mg), cation exchangeable capacity (CEC), and base saturation percentage (BS%) were measured using the ammonium acetate method at pH 7 [24]. Mehlich-3 extraction [25] was used for analysis of plant available nutrients. Mehlich-3 extractable (M3-) K, Na, Ca, Mg, Fe, Mn, Cu, Pb, Zn, and P values were measured with ICP-OES.

2.2. Studied BC

BC produced from lead tree (*Leucaena leucocephala* (Lam.) de. Wit) in an earth kiln was constructed by the Forest Utilization Division, Taiwan Forestry Research Institute, Taipei, Taiwan [26,27]. The charring for earth kilns typically requires several days and reaches temperatures of 500 °C to 700 °C. The highest temperature in the kiln at the end of carbonization was above 750 °C. The BCs were homogenized and ground to <2 mm mesh for analyses. The characterization of the studied BC was described in previous studies [28,29] (Table 1).

2.3. Incubation Experiment

To investigate the effect of biochar on C mineralization of compost excessive application soils, in this study, 5% commercially available swine manure compost was added as a soil fertilizer, which is twice the recommended amount of organic fertilizer in Taiwan. The economic viability of 5% manure compost is highly unlikely for most farmers, but that is not the objective of the present work.

In amended soils, laboratory incubation is generally used to obtain accurate information about C-mineralization dynamics [30], and the data can then be fitted to or with kinetic models to obtain complementary information, such as C-mineralization rates and the potentially mineralizable C. Therefore, a laboratory aerobic incubation experiment was conducted over 434 days to study and evaluate C-mineralization kinetics in a non-amended (no BC addition) soil sample (i.e., the control) and in three soils amended with three BC application rates. A total of 12 treatments were used in this study, and each treatment was set in five replicates. The application rate of BC, 0%, 0.5%, 1.0%, and 2.0% (*w/w*), equated to field applications of approximately 0, 9, 18, and 36 tons/ha, respectively, considering 1800 Mg of soil per hectare (soil bulk density equal to 1.2 Mg/m³ and an arable soil layer of 15 cm). Twenty-five grams of mixed soil sample was placed in 30-mL plastic containers, which were subsequently put into 500-mL plastic jars containing a vessel with 10 mL of distilled water to avoid soil desiccation, and a vessel with 10 mL of 1 M NaOH solution to trap evolved CO₂. The jars were sealed and incubated at 25 °C. Soil moisture content was adjusted to 60% of field capacity before the incubation and was maintained throughout the experiment using repeated weighing. The incubation experiment was run for 434 days with 23 samples taken after 1, 3, 7, 14, 21, 28, 35, 42, 49, 56, 63, 77, 91, 105, 119, 133, 161, 189, 217, 245, 308, 371, and 434 days. After sampling, the vessel with 10 mL of 1 M NaOH solution was removed, resealed, and stored until analysis for CO₂ and replaced with fresh NaOH. A titrimetric determination method was used to quantify the evolved CO₂ [31]. The cumulative CO₂ released and C mineralization kinetics were calculated based on the amount of CO₂-C released during different intervals of time in each treatment. In addition, total mineralization coefficient (TMC) was calculated according to Díez et al. [32] and Méndez et al. [33], as follows:

$$\text{TMC (mg CO}_2\text{-C/g C)} = \text{CO}_2\text{-C evolved/initial TOC} \quad (1)$$

where CO₂-C evolved is expressed as mg CO₂-C/100 g soil and initial total organic carbon (TOC) is expressed as g C/100 g soil.

Samples of the BC-treated soil were collected after incubation for 434 days or analysis of plant available nutrients using Mehlich-3 extraction (M3-) [25]. M3-K, Na, Ca, Mg, Fe, Mn, Cu, Pb, Zn, and P values were measured with ICP-OES. To compare the changes and quantify the impacts of soil BC amendments on nutrients, soil pH, TC, TN, TP, exchangeable bases (Ex-K, Na, Ca, Mg), and CEC of the BC-treated soil on day 434 were also measured.

2.4. Statistical Analysis

The statistical analyses (calculation of means and standard deviations, differences of means) were performed using SAS 9.4 package (SAS Institute, Inc., SAS Campus Drive, Cary, NC, USA). The results were analyzed by analysis of variance (one-way ANOVA) to test the effects of each treatment. The statistical significance of the mean differences was determined using least-significant-difference (LSD) tests based on a *t*-test at a 0.05-probability level. The Pearson correlation coefficient (*r*) was calculated and principle component analysis (PCA) was performed using SAS 9.4 software. The multivariate statistical technique of PCA was used to investigate the most susceptible variances and to identify the important components explaining most of the variances in a large data set.

3. Results

3.1. Carbon Mineralization

The addition of woody BC showed significantly reduced CO₂ release in SAO soil, no significantly difference in MAI soil, and a significant increase in SAI soil (Figure 1 and Table 2). In SAO soil treatments, the CO₂-C release reduced by about 8.8%, 7.0%, and 9.4% for 0.5%, 1.0%, and 2.0% BC addition rates, respectively. No significant difference was observed in the MAI soil treatments; the CO₂-C release reduced by about 8.8%, 7.0%, and 9.4% for 0.5%, 1.0% and 2.0% BC addition rates, respectively. In contrast, in SAI soil treatments, the CO₂-C release increased by about 6.2%, 15.3%, and 7.9% for 0.5%, 1.0%, and 2.0% BC addition rates, respectively. The results of total mineralization coefficient (TMC) indicated a significantly reduced trend with increasing BC addition in SAO and MAI soil treatments; however, in SAI soil, only the 2% addition showed a significantly decrease, in comparison with the control. The value of TMC was higher in SAI soil treatments, followed by MAI soil treatments, and much lower in SAO soil treatments. The TMC value decreased by 16.5%, 24.0%, and 37.8% for 0.5%, 1.0%, and 2.0% BC additions to SAO soil, respectively. In MAI soil, TMC reduced by 19.6%, 20.7% and 32.5% for 0.5%, 1.0%, and 2.0% BC additions, respectively. In SAI soil, TMC reduced by 0.7% and 19.8 for 0.5% and 2.0% BC addition, respectively, but increased by 2.0% for 1.0% BC addition. We hypothesized that woody BC addition may stabilize compost organic matter and diminish C mineralization in soils with excessive compost application, and the results showed that addition of woody BC to SAO soil produced a favorable effect by decreasing the cumulative amount of CO₂-C evolution, but in SAI soil, it produced an unfavorable effect by increasing the cumulative amount of CO₂-C evolution. We observed no effect in MAI soil.

Table 2. CO₂-C evolved (mg C/100 g dry weight) and total mineralization coefficient (TMC) for control and amended soils after the incubation experiment ¹.

Rate	CO ₂ Evolved (mg C/100 g Dry Weight)	TMC (mg CO ₂ -C/g C)
SAO Soil		
0%	842 ± 8.7 A	333 ± 3.4 A
0.5%	768 ± 18 B	278 ± 6.4 B
1.0%	783 ± 15 B	253 ± 4.7 C
2.0%	763 ± 21 B	207 ± 5.7 D
MAI Soil		
0%	829 ± 30 A	526 ± 19 A
0.5%	782 ± 18 A	423 ± 9.6 B
1.0%	797 ± 17 A	417 ± 8.7 B
2.0%	803 ± 10 A	355 ± 4.5 C
SAI Soil		
0%	692 ± 20 C	455 ± 14 A
0.5%	735 ± 18 BC	452 ± 11 A
1.0%	798 ± 24 A	464 ± 14 A
2.0%	747 ± 10 B	365 ± 4.9 B

¹ Each value is the average ± standard deviation from three independent experiments. Means compared within a column, followed by a different uppercase letter, are significantly different at $p < 0.05$ using a one-way ANOVA (multiple comparisons vs. studied soil + 0% biochar as a control).

Figure 1. Cumulative CO₂-C (mg CO₂-C/100 g soil) from the three studied soils treated with 0%, 0.5%, 1.0%, and 2.0% woody biochar. Error bars indicated standard deviation of the mean.

3.2. Changes in Soil Properties and Fertility Characteristics

After 434 days of incubation, all treatments were analyzed to investigate if BC addition could result in increasing (enhancing) or decreasing (reducing) soil properties and fertility characteristics in compost over-applied soils (Table 3). The enhancing effect on soil fertility characteristics suggests that adding BC can retain nutrients in compost over-applied soils, even after one year of incubation. The high amount of nutrients retained in the soils at the end of the study period suggests that the farmer could apply less compost in the following year.

Table 3. Mean values of total soil carbon (TC), nitrogen (TN), and phosphorus (TP), soil pH, exchangeable bases (K, Na, Ca, and Mg), and cation exchangeable capacity (CEC) of four treatments of three soils after 434-day incubations ¹.

Rate	pH	Ex-K	Ex-Na	Ex-Ca	Ex-Mg	CEC	TC	TN	TP	C/N
-----coml(+)/kg soil-----						-----g/kg-----				
SAO Soil										
0%	5.66 b	2.55 b	0.72 b	14.9 a	3.58 a	16.4 a	23.9 c	4.37 ab	1.55 c	5.5 c
0.5%	5.75 b	2.87 a	0.91 a	15.0 a	3.73 a	16.4 a	28.0 b	4.43 a	1.77 b	6.3 b
1.0%	5.76 b	2.40 b	0.73 b	14.4 a	3.36 a	16.0 a	31.8 a	4.28 b	1.69 bc	7.4 a
2.0%	5.93 a	2.55 b	0.63 b	15.5 a	3.41 a	16.3 a	34.5 a	4.27 b	2.21 a	8.1 a
MAI Soil										
0%	7.53 c	2.64 b	0.66 a	22.9 a	3.37 a	9.7 b	18.2 c	3.64 b	0.88 bc	5.0 c
0.5%	7.58 b	2.92 b	0.68 a	25.5 a	3.78 a	10.1 b	21.9 b	3.62 b	0.75 c	6.0 bc
1.0%	7.58 bc	2.92 ab	0.68 a	25.5 a	3.78 a	10.7 a	22.2 b	4.06 a	1.05 ab	5.5 b
2.0%	7.65 a	3.24 a	0.76 a	25.9 a	3.75 a	10.0 b	32.4 a	4.15 a	1.18 a	7.8 a
SAI Soil										
0%	7.04 c	2.14 c	0.59 a	13.9 a	4.24 a	13.4 a	13.7 c	2.86 b	1.26 a	4.8 c
0.5%	7.11 b	2.30 bc	0.54 a	15.3 a	4.52 a	13.3 a	18.3 b	2.89 b	1.11 a	6.3 b
1.0%	7.14 b	2.61 a	0.62 a	15.6 a	4.56 a	13.6 a	21.4 b	3.06 a	0.88 b	7.0 b
2.0%	7.24 a	2.45 ab	0.54 a	14.9 a	4.23 a	12.8 b	26.6 a	3.07 a	0.64 c	8.7 a

¹ Each value is the average of three independent experiments. Means compared within a column followed by a different lowercase letter are significantly different at $p < 0.05$ using a one-way ANOVA (multiple comparisons vs. studied soil + 0% biochar as a control).

At the end of incubation, TC significantly increased with increase of BC addition in the three soils. The significant decreases in CO₂-C evolution and TMC with BC addition increase explain the soil carbon accumulation (sequence) in soils. That is, in this study, BC addition evidently reduced C-mineralization and TMC, and resulted in more soil C sequestered in soils. TN content significantly increased with 1% and 2% BC addition in MAI and SAI soils, but slightly decreased in SAO soil. The application of woody BC with a high C/N ratio in three soils did not obviously result in soil nitrogen fixation, but in contrast, increased TN content. The TP content significantly increased with 0.5% and 2.0% BC addition in SAO soil and with 2.0% in MAI soil, but significantly decreased with 1.0% and 2.0% BC addition in SAI soil. The C/N ratio significantly increased with BC addition increase, the values of which were all less than 10:1 (Table 3).

Soil pH significantly increased with 2.0% BC addition of three soils—about 0.3 pH unit for SAO soil, 0.1 pH unit for MAI soil, and 0.2 pH unit for SAI soil (Table 3). Within the exchangeable bases, Ca and Mg showed insignificant difference from the control in the three soils, but obviously increased in the MAI and SAI soils. The addition of 0.5% BC resulted in a significant increase in the K and Na contents in SAO soil but a decrease with 1.0% and 2.0% additions. The 2% BC addition in MAI, and 1.0% and 2.0% BC additions in SAI soil significantly increased K content. CEC showed variable changes—significant increases occurred in 1.0% BC addition to MAI soil but significant decreases occurred with 2.0% addition to SAI soil.

In SAO soil, in terms of soil fertility characteristics, M3-P, K, Mg, Fe, and Mn content obviously and significantly decreased with increasing BC addition (Table 4). In contrast, Ca, Cu, Pb, and Zn content increased with increasing BC addition, especially with the 2.0% addition. The amount of Cu,

Pb, and Zn in SAO soil was about 8–9, 10–12, and 26–30 mg/kg, respectively. These values are not very high and cannot result in plant toxicity. However, we should pay more attention to SAO soil, to ensure that these metals are not fixed by BC, and their availability may increase after BC addition. In MAI soil, the amount of P, K, Ca, Mg, Fe, and Mn increased after BC addition, but only K content significantly increased with 1.0% and 2.0% BC addition. Significant decreases of Cu, Pb, and Zn occurred with 0.5%, 1.0%, and 2.0% BC addition (except for Zn with 2.0%). The application of woody BC in MAI soil can help retain some nutrients and significantly reduce heavy metal availability. Similar results for K, Cu and Pb were found for SAI soil. However, P content with 1.0% BC addition and Zn content with 0.5% and 1.0% addition was significantly increased in SAI soil. Ca, Mg, Fe, and Mn content decreased after BC addition. Adding BC to SAI soil could result in some nutrient decrease and reduce the availability of Cu and Pb, but we should pay attention to the risk of increased Zn availability.

Table 4. Mean values of soil fertility characteristics (Mehlich 3 extraction) (mg/kg) of four treatments of three soils after 434-day incubations ¹.

Rate	P	K	Ca	Mg	Fe	Mn	Cu	Pb	Zn
SAO Soil									
0%	645 a	461 a	2701 b	533 a	953 a	5.7 ab	8.64 c	10.3 b	26.8 b
0.5%	653 a	467 a	3216 a	556 a	948 a	37.2 a	9.02 bc	10.2 b	28.6 b
1.0%	486 b	408 b	3118 a	444 b	739 b	31.6 c	9.36 ab	11.0 b	27.8 b
2.0%	537 b	457 a	3188 a	474 ab	777 b	3.5 bc	9.83 a	12.3 a	30.6 a
MAI Soil									
0%	769 ab	474 c	7594 a	636 ab	694 ab	286 a	8.73 a	12.9 a	12.2 a
0.5%	671 b	481 bc	7799 a	611 b	621 b	271 a	7.79 b	11.4 b	10.6 b
1.0%	832 a	545 a	7142 a	712 a	739 a	310 a	7.60 b	10.7 b	10.3 b
2.0%	795 a	534 ab	7697 a	660 ab	707 ab	301 a	7.66 b	11.3 b	11.1 ab
SAI Soil									
0%	476 b	384 c	3569 a	750 a	1257 a	197 a	1.70 a	0.84 a	9.48 c
0.5%	462 b	392 bc	3292 a	712 a	1147 a	186 a	1.66 a	0.67 ab	10.1 b
1.0%	564 a	474 a	3313 a	759 a	1200 a	196 a	1.54 b	0.57 bc	11.1 a
2.0%	470 b	437 ab	3648 a	726 a	1183 a	194 a	1.29 c	0.48 c	9.53 bc

¹ Each value is the average of three independent experiments. Means compared within a column followed by a different lowercase letter are significantly different at $p < 0.05$ using a one-way ANOVA (multiple comparisons vs. studied soil + 0% biochar as a control).

3.3. Principal Component Analysis

The PCA described substantial differences in soil physicochemical characteristics (pH, TC, TN, TP, M3-P, M3-K, M3-Cu, M3-Pb, and M3-Zn), and cumulative CO₂-C among the BCs (Figure 2). The PCA identified two primary components of SAO soil fertility, and PC1 and PC2 accounted for 49.1% and 21.0% of the total variance, respectively. AdditioPC1 and PC2 explained 43.0% and 19.8%, and 52.3% and 23.3% of the total variance in the MAI and SAI soil, respectively.

PCA showed two groupings for each of the three soils. The two grouping of SAO soil were: pH, TC, TP, M3-Pb, M3-Zn, and M3-Cu (Group 1); and TN, M3-P, M3-K, and cumulative CO₂-C (Group 2). The 2% BC addition was clustered near Group 1, whereas the 0.5% BC addition was clustered closer to Group 2. For the MAI soil, two groupings stood out: pH, TC, TN, TP, M3-P, and M3-K (Group 1); and M3-Cu, M3-Pb, M3-Zn, and cumulative CO₂-C (Group 2). The addition of 1% BC was clustered near Group 1. Lastly, the PCA for the SAI soil showed two main groupings: pH, TC, TN, M3-P, M3-K, M3-Zn, and cumulative CO₂-C (Group 1); and TP, M3-Cu, and M3-Pb (Group 2). Addition of 1% BC was clustered closer to Group 1, whereas 0.5% BC addition was clustered closely to Group 2.

Figure 2. Principal component analysis based on soil chemical characteristics and cumulative $\text{CO}_2\text{-C}$ (mg $\text{CO}_2\text{-C}/100\text{g}$ soil) after 434-d incubation period in SAO, MAI, and SAI soils treated with 0%, 0.5%, 1.0%, and 2.0% woody BC.

4. Discussion

4.1. Effect of BC on Carbon Mineralization

While proper use of compost promotes soil productivity and improves soil quality, excess application degrades soil and water quality, and inhibits crop growth [34]. The net decrease in CO_2 emission with BC is clear, both directly through sequestration of BC-C and indirectly by altering the soil's physical, chemical, and microbiological properties [5,35]. The BC used in our study was a high-temperature pyrolysis product of wood with an accumulation of black C. This property makes it inert and resistant to microbial degradation [36]. In this study, we hypothesized that the addition of relatively small amounts of woody BC to soils with excess swine manure compost application could stabilize compost organic matter and decrease C mineralization. Decreasing C mineralization could contribute to reducing the decomposition of compost organic matter, enhance C sequestration, retain some nutrients, and may reduce the application rate of manure compost in the following year.

Carbon mineralization in each soil type was obviously greater in the initial days of incubation (Figure 1), especially on the first day, as reported in other studies [37–39]. Swine manure compost contains a significant amount of easily degradable organic C, and consequently, intense increases in soil

microbial activity should occur after its application to soil, leading to high C mineralization. The BC treatments significantly reduced C mineralization in SAO soil, and showed insignificant difference in MAI soil (Table 2), but significantly increased C mineralization in SAI soil (1.0% and 2.0% BC treatments). Mukome et al. [40] showed that emissions of CO₂ from the interaction of BC with compost organic matter (COM) are dependent on the BC feedstock and pyrolysis temperature; however, net CO₂ emissions were less for the BC and compost mixtures compared to compost alone, suggesting that BC may stabilize COM and diminish C mineralization. The presence of easily metabolized organic C or additional labile organic carbon sources has been shown to accelerate BC decomposition (or increased soil CO₂ effluxes) [41–44], suggesting that co-metabolism contributes to BC decomposition in soils. Respiration per unit of TOC (TMC) of the three studied soils significantly decreased with increasing BC addition. The four treatments in SAO soil had significantly lower TMC than in MAI and SAI soils. Méndez et al. [33] suggested that a high TMC results in a more fragile humus and thus in a lower quality soil. In contrast, the lower TMC means that organic matter is conserved more efficiently and maintains activity of the microorganisms responsible for soil organic matter biodegradation.

BC amendments clearly have effects on soil CO₂ evolution, which vary with soil type. In coastal saline soil (pH 8.09), peanut-shell-derived BC addition increased the cumulative CO₂ emissions and the cumulative SOC mineralization due to labile C released from BC and enhanced microorganism proliferation [37]; however, the increased mineralized C only accounted for less than 2% in the 0.1%–3% BC treatments, indicating that BC may enhance C sequestration in saline soil. Rogovska et al. [14] indicated that BC additions sometimes increase soil respiration and CO₂ emissions, which could partially offset C credits associated with soil BC applications, and many uncertainties are related to estimation of mineralization rates of BC in soils. In this study, the result of CO₂ evolution and TMC both suggest that when adding excess swine manure compost to Oxisols, a higher BC application rate can stabilize and prevent rapid mineralization of compost. BC addition in mildly alkaline Inceptisols can stabilize compost organic matter, but only slightly decrease mineralization of the compost. In slightly acid Inceptisols, a higher BC application rate can stabilize compost organic matter but may significantly increase mineralization of the compost.

4.2. Effect of BC on Soil Properties and Fertility Characteristics

In the tropics, natural rapid mineralization of soil organic matter is a limitation of the practical application of organic fertilizers, despite it enhancing soil fertility [34]. Thus, the repeated application of organic materials at high doses can significantly contribute to global warming, plant toxicity, accumulation of heavy metals in plants, and ground and surface water pollution due to nutrient leaching. Some studies have indicated that the simultaneous application of BC and compost resulted in enhanced soil fertility, water holding capacity, crop yield, and C sequestration [45–48]. Schulz and Glaser [48] found that overall plant growth and soil fertility decreased in the order of compost > BC + compost > mineral fertilizer + BC > mineral fertilizer > control. The combination of BC with mineral fertilizer further increased plant growth during one vegetation period but also accelerated BC degradation during a second growth period. A combination of BC with compost showed the best plant growth and C sequestration, but had no effects on N and P retention. The blending of BC with compost has been suggested to enhance composting performance by adding more stable C and creating a value-added product (BC-compost blend) that can offset both the potential negative effects of the composting system and the pyrolysis BC system [16].

In addition to diminishing C mineralization in soils, we further examined the positive or negative effects of soil nutrients and heavy metals on mineralization and availability after 434 days of incubation. The results suggested that the effects of adding woody BC vary with soil type and element (Table 4). Without amendment with compost, the soils used in this study had low plant available contents of some nutrients, as well as low CEC. Soils with low CEC are often not fertile and are vulnerable to soil acidification [47]. The CEC of the studied soils followed the order: SAI soil > MAI soil > SAO soil. After incubation, the soil pH of the four treatments in SAO soil (Table 3) were lower than in bulk soil

(Table 1), suggesting low soil buffering capacity, and that soil acidification occurred after adding excess manure compost. In Dystric Cambisol with a loamy-sand texture, a maize (*Zea mays* L.) field trial with five treatments (control, compost, and three BC-compost mixtures with constant compost amount (32.5 Mg/ha) and increasing BC amount, ranging from 5–20 Mg/ha) was conducted [13]; the results demonstrated that total organic C content could be increased by a factor of 2.5 from 0.8% to 2% ($p < 0.01$) at the highest BC-compost level, compared to the control. TN content only slightly increased and plant-available Ca, K, P, and Na content increased by factors of 2.2, 2.5, 1.2, and 2.8, respectively. Trupiano et al. [15] indicated that, when compared to the addition of compost alone, the compost and BC combination did not improve soil chemical characteristics, except for an increase in total C and available P content. These increases could be related to BC capacity to enhance C accumulation and sequestration, and to retain and exchange phosphate ions by its positively charged surface sites. Oldfield et al. [16] suggested that BC recycles C and P; whereas compost recycles C, N, P, and K; and a blend of both resulted in the recycling of C, N, P, and K. Regional differences were found between BC, compost, and the BC-compost blend, and the BC-compost blend offered benefits in relation to available nutrients and sequestered C [16].

4.3. BC Addition Rate Effects on Soil Carbon Mineralization and Soil Fertility

Deteriorating soil fertility and the concomitant decline in agricultural productivity are major concerns in many parts of the world [46]. It is a critical problem in Taiwan. Biochar and biochar-compost applications positively impact soil fertility, for example, through their effect on SOC, CEC, and plant available nutrients [45]. Naeem et al. [49] suggested that the application of BC, in combination with compost and inorganic fertilizers, could be a good management strategy to enhance crop productivity and improve soil properties. Agegnehu et al. [46] indicated that as the plants grew, compost and biochar additions significantly reduced leaching of nutrients; separate or combined application of compost and biochar together with fertilizer increased soil fertility and plant growth. The application of compost and biochar improved water and nutrient retention in the soil, and thereby the uptake of water and nutrients by the plants [46]. The application of woody BC has potential for stabilizing compost organic matter, diminishing soil C mineralization, and improving soil nutrient availability in soil with excessive compost application, depending on soil type and application rate. Addition of BC in SAO soil and MAI soil led to substantial improvements in physicochemical properties, as well as significant and insignificant lower C mineralization, respectively (Figure 1 and Table 2). The 0.5% BC addition reduced the content of available P and K, and 2% addition could result in the risk of Cu, Pb, and Zn in SAO soil. In MAI soil, 1% addition increased pH and content of TC, TN, TP, M3-P, and M3-K. In contrast, BC addition in SAI soil resulted in significant higher C mineralization. The addition of 1% BC increased in soil pH and the contents of TC, TN, M3-P, M3-K, and M3-Zn, but 0.5% BC addition would reduce the contents of TP, M3-Cu, and M3-Pb.

PCA of the soil properties measured by Speratti et al. [50] found that both BC feedstocks had positive correlations between Ca, Fe, and Mn. Metals such as Fe and Mn, along with lower soil pH, can contribute to the formation of organo-mineral and/or organo-metallic associations that decrease BC mineralization [51]. This can increase BC-C stability in the soil, which may improve soil structure [52]. In this study, the free Fe oxide (dithionate-citrate-bicarbonate extractable) content was very high (43.1 g/kg) in SAO soil, followed by MAI soil, and SAI soil at 8.80 g/kg and 6.96 g/kg, respectively. Along with lower soil pH (<pH 6.0), BC, compost, and soil Fe oxide can contribute to the formation of organo-mineral and/or organo-metallic associations that improve soil structure, stabilize compost organic matter, and decrease mixed-soil C mineralization in SAO soil. The soil pH in MAI soil was highest. The potential of BC to reduce C mineralization in MAI soil was insignificant between the control and BC treatments but showed minor reductions after BC addition treatments. After BC addition, the mixed-soil C mineralization significantly increased, which could contribute to lesser formation of organo-mineral and/or organo-metallic associations due to the lower amount of Fe oxides and higher soil pH (7.1–7.2). Adding two biochars at 2% (*w/w*) composed of lac tree wood and mixed

wood (scrapped wood and tree trimmings), with and without vermicompost or thermocompost at 2% (*w/w*) in Hawaii in highly weathered soils (Ultisols and Oxisols), Berek et al. [53] indicated that soil acidity, nutrient in the soils, plant growth, and nutrient uptake improved with the amendments compared to the control. Nutrient increases and soil acidity reduction by additions of biochar combined with compost were the probable cause, and the use of locally produced biochars and composts was recommended to improve plant nutrient availability in highly weathered soils [53].

5. Conclusions

In this study, we assessed the capacity of woody BC in soils with excessive compost application to stabilize compost organic matter, diminish C mineralization, and improve nutrient availability in three highly frequent tillage soils in Taiwan (Oxisols, SAO; and Inceptisols, MAI and SAI). The effect of BC addition varied strongly according to soil type. Soil carbon mineralization significantly decreased with increasing BC addition in SAO soil, and produced insignificant changes in MAI soil, but significant increases in SAI soil. Respiration per unit of TOC (TMC) significantly decreased with increasing BC addition. In this study, a higher BC application rate stabilized and prevented the rapid mineralization of swine manure compost. Soil pH, exchangeable bases, and CEC only showed minor increases with increasing BC addition. BC addition had a positive effect on soil fertility, including TC, TN, TP, M3-P, K, Mg, Fe, Mn, Pb, and Zn, but had slightly positive effect on exchangeable Ca and negative effect on extractable Cu. To improve soil nutrient availability, adding BC generally increased the levels of plant macronutrients and reduced the concentrations of micronutrients. The results of PCA, even with low scores, indicated that adding BC has a positive impact on diminishing soil carbon mineralization (carbon sequestration), sustaining soil fertility, and preventing heavy metals contamination in compost over-applied soil. In this study, 1% biochar addition corresponds to 18 tons/ha. As adding a large amount of biochar in open fields would be unrealistic and not economically sustainable, we suggested that adding 0.5% woody BC to three studied soils should be reasonable and appropriate.

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